Electro-Aggregation of Asphaltene Particles

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Formation and deposition of heavy organic compounds of petroleum fluids including, but not limited to, asphaltene particles in oil well columns and production systems, are important flow assurance problems in both onshore and offshore operations. Therefore, preventive actions to control asphaltene deposition and remediation of such heavy organic deposit, which leads inevitably to reduction or cessation in oil production, has been always one of the main concern for oil producers. In this work, the effect of electrostatic field on the aggregation rate and aggregate size of asphaltene particles precipitated out from crude oil samples suspended in the mixture of toluene and n-heptane has been investigated. Electrode embedded glass micro-model equipped with high resolution optical microscope and high voltage direct current power supply has been utilized to perform the experiments. The asphaltene particle size and the rate of aggregation under the electric field has been monitored using a high resolution microscope and the average aggregate size for asphaltene particles have been measured using image processing software. It has been concluded that the asphaltene aggregation rate and the average diameter of asphaltene aggregates not only depend on the molecular structure and the number of hetero-atoms on asphaltene molecules but also can be significantly affected by the electric field strength, exposure time, asphaltene concentration and the amount of precipitant i.e., n-heptane. As a matter of fact, under the electrostatic field, asphaltene particles tend to become highly polarized and oriented, and thus, to aggregate more quickly. Such kinetic behavior, in turn, may result in asphaltene deposition. The application of the electrostatic technique to control asphaltene deposition in a pipeline has been also discussed.
Viscosity Modeling of Ionic Solutions

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In the present work, an Eyring-theory model based on concepts of excess Gibbs energy of activation of the viscous flow has been developed for the accurate correlation and/or prediction of the dynamic viscosity of ionic solutions: inorganic salt (electrolyte) + solvent and organic salt (ionic liquid) + solvent. For the excess Gibbs energy of activation ($G^{\text{ex}}_\text{Eyr}$), both thermal and mechanical contributions to the viscous flow were considered. Accordingly, a thermal $G^{\text{ex},T}_\text{Eyr}$ term was described by mixing rules of the Redlich-Kister type whereas the mechanical $G^{\text{ex},\tau}_\text{Eyr}$ term was computed from a simple cubic equation of state in an attempt to overall represent the main molecular interactions (between the ionic species and the solvent) affecting viscosity. The resulting model was successfully validated during the representation of experimental dynamic viscosities of various non-aqueous and aqueous ionic solutions within wide ranges of temperature, pressure and composition (or salt molality).
We describe novel theoretical techniques for modeling and understanding the radiative properties of highly inhomogeneous and nonlinear nanostructured materials. To begin with, we demonstrate that powerful methods based on the volume-integral formulation of electromagnetic scattering can be readily extended to study not only thermal radiation, but also fluorescence and spontaneous emission from wavelength-scale bodies with large thermal gradients and/or inhomogeneous dielectric permittivities. We show that if properly formulated, the volumetric scaling of these methods is not an impediment to large-scale thermal radiation calculations of bodies with arbitrary shapes and materials, a consequence of the rank-deficient nature of the underlying scattering matrices. Moreover, we demonstrate that one can exploit these techniques to obtain the far-field modal contributions to the thermal radiation of complex bodies, paving the way for potential design methodologies that exploit robust and increasingly powerful large-scale optimization techniques. We illustrate these features by presenting results in a number of new structures. Time permitting, we will switch gears and describe an entirely different set of problems involving nano-structured materials designed to enhance the interaction of thermal radiation with material nonlinearities. Such materials can no longer be described via the well-known fluctuation-dissipation theorem of linear materials, and can lead to various temperature-tunable phenomena, including strong spectral alterations and enhanced thermal radiation at selective wavelengths, even exceeding the black body radiation for bodies out of equilibrium.
Lately, several experimental studies have shown that ionic liquids exhibit, among other thermophysical properties, high gas solubilities. Accordingly, the use of an ionic liquid as gas separation media seems to be very promising particularly for the capture/sequestration of ammonia which has shown to be extremely soluble in ionic liquids as compared to other gases. Recently, several experimental works have appeared in the literature dealing with the solubility of ammonia in imidazolium-based ionic liquids at different temperature and pressure conditions. The purpose of this work is to present a formal modeling approach of the ammonia solubility in ionic liquids by the use of a cubic equation of state (Soave or Peng-Robinson) coupled with modern mixing rules of the Wong-Sandler type. The resulting modeling approach proves to be able to correlate and/or predict the ammonia solubility in ionic liquids over diverse conditions of temperature, pressure and solute composition.
Equation of State and Phase Behavior of a Difluoromethane - Pentafluoroethane Mixture

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Binary mixture of difluoromethane (R32) and pentafluoroethane (R125) corresponds to the requirements for new ozone-safe refrigerants. Therefore we derived the equation of state on the basis of experimental data for this mixture by method of Lemmon and Jacobsen (1999). The experimental data for mixture R32/R125 include 2973 \( p, ρ, T, x \) points from 18 sources at 200-400 K and 0.02-39 MPa for 19 values of composition, 302 points in saturation from 10 sources at 205-340 K for 29 compositions and 388 values of isochoric heat capacity at 207-397 K and 4-33 MPa. For satisfaction of phase equilibrium condition data on 43 isotherms at 223-340 K were used. At calculations the reliable equations of state for the components were used. The coefficients of interaction function for mixture were defined on the basis of step-wise regression analysis proposed by Reuck and Armstrong (1979). The root mean square deviation of density values calculated by compiled equations of state from experimental data is equal 0.25% and of \( c_v \) values — 1.10 %. Thermodynamic properties of mixture were calculated by equation of state for four values of composition for the temperatures 200-400 K and pressures 0.1-39 MPa. The \( ρ, T, x \) diagram was plotted in order to analyze the thermodynamic behavior of the R32/R125 mixture at the phase equilibrium state. The temperature differences of saturated vapor and liquid on isobars were analyzed in order to estimate quantitatively the behavior of this mixture in the saturation state at various compositions. This enables to maintain optimum values of the temperature difference between water or air and refrigerant upon its condensation and between a cooled object and vaporizing refrigerant. The analysis shows, that this mixture is applicable as refrigerant over a wide range of compositions.
$^1$H NMR and Acoustic Response of Binary Mixtures of an Organophosphorous Extractant with 1-Alkanols (C$_1$–C$_4$, C$_8$)

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Density ($\rho$), ultrasonic velocity ($U$) and viscosity ($\eta$) of an organophosphorous extractant, i.e. di (2-ethylhexyl) phosphoric acid (D2EHPA) and its binary mixtures with five alkanols (C$_1$–C$_4$, C$_8$) viz., methanol, ethanol, 1-propanol, 1-butanol and 1-octanol have been measured at 303.15 K and atmospheric pressure. Using these experimental values, excess molar volume , excess Gibbs free energy of activation, deviations in ultrasonic velocity, viscosity, isentropic compressibility, intermolecular free length and acoustic impedance have been computed over entire mole fraction range of D2EHPA. These excess / deviation functions were fitted to Redlich-Kister type of polynomial equation to derive binary coefficients and estimate standard errors between the experimental and calculated data. The result of the above deviation/excess functions i.e. macroscopic properties of the binary mixtures (1-alkanol + D2EHPA) suggest the presence of stronger molecular interaction between unlike molecules which gradually decreases with increase of carbon chain of 1-alkanol. Furthermore, $^1$H NMR spectra of these binary mixtures at a constant volume have been reported. Microscopic property such as chemical shift is obtained from $^1$H NMR spectral analysis in all studied mixtures. Comparison of macroscopic and microscopic properties reveals that dipole-dipole type of molecular interaction between dissimilar molecules in D2EHPA and 1-alkanol system predominates over others and degree of interaction is relatively stronger in methanol may be due to its smaller carbon chain length and higher dielectric constant.
Hydrocarbons with cyclic structures (naphthenic and aromatic) make up a significant share of the hydrocarbon composition of oil and gas condensates, and are important for chemical technology. For the lighter aromatic and naphthenic hydrocarbons, a fundamental equation of state, which allows the calculation of all thermodynamic properties, has been developed. Reliable experimental data are not readily available for more complex hydrocarbons, and it is not always possible to develop dedicated equations of state for each compound. Thus, the development of a generalized equation is a good alternative. A critical analysis and selection of the most reliable experimental data for thermodynamic properties of naphthenic and aromatic hydrocarbons was made by the authors. The lack of experimental data in some regions of the state parameters was filled by calculated data. The inclusion of calculated data in the fitting procedure increased the stability of the equation and improved the extrapolation behavior. These data were included in the fitting procedure with small weights. The generalization is made possible through a framework of the extended three-parameter corresponding states principle. This equation is explicit in the reduced Helmholtz free energy, with the reduced density, reduced temperature, and acentric factor as independent variables. The acentric factor was chosen as the determining criterion of similarity. To describe the residual part of the reduced Helmholtz energy, an optimized functional form developed by Sun and Ely was used. This form was successfully used in previous work by the authors to develop a generalized equation of state for n-alkanes. Optimization of the coefficients and temperature exponents of the proposed equation took place simultaneously in a nonlinear form. The proposed equation has enough precision to calculate thermodynamic properties and phase behavior of the investigated hydrocarbons over a range of the acentric factor $\omega = 0.2 – 1.1$ and over a temperature range from the triple point to 700 K with pressures up to 100 MPa.
Thermophysical Data Based Parameters of Pair Molecular Interactions in Real Gases

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The databases of thermophysical properties are widely used in practice to model and control various technological processes. Much less is known about them as sources of fundamental knowledge concerning molecular interactions. The report demonstrates a new method of the pair molecular interaction parameters extraction from the NIST Thermophysical Properties of Fluid Systems Database.

First, we find the pair interaction energy $E_{2i}$ in Kelvin from the constant volume heat capacity $C_v$ and the internal energy $U$ of a diluted pure real gas:

$$E_{2i} = -T \frac{\partial C_v}{\partial U} |_{T}.$$  

The pair interaction energy $E_{2i}$ includes the dimer bond energy $E_2$ and monomer-monomer repulsion energy $E_{2mr}$. For many investigated gases the monomer repulsion energy is proportional to temperature $T$ with a slight quadratic nonlinearity. This fact permits to find the dimer bond energy by excluding the $E_{2mr}$ from the pair interaction energy.

In this method the dimer bond parameters are:

- The dimer bond energy $E_2$, considered as the thermodynamics average energy for dimers dissociation;
- The equilibrium constant $C_{u2}$, reflecting the dimer fraction contribution in the internal energy of a real gas;
- The thermodynamically averaged volume of the dimer attraction zone:
  $$V_2 = C_{u2} / \exp\left(E_2 / T\right);$$
- The excluded volume, $V_{ex}$;
- The effective volume $V_{rep}$ for monomer-monomer repulsions:
  $$V_{rep} = -T \frac{dV_{ex}}{dT}.$$ 

At high temperatures the dimer bond energy $E_2$ and the volume of the dimer attraction zone $V_2$ tend to be constant, but at low temperatures they change noticeably, thus reflecting the solidification of dimers near the triple point.

The report demonstrates the dimer bond parameters for a number of pure atomic, polar and non-polar molecular gases.
Clusters’ Bond Energies and Pores’ Energy Deficits in Near Critical Fluids

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The fluids are essentially heterogeneous, what appears as the critical opalescence at the critical point, where dimensions of clusters and pores approach the visible light wavelength. An absence of the opalescence at larger distances from the critical point does not mean an absence of clusters or pores in a fluid. To visualize smaller clusters and pores we should use much shorter wavelengths. The Keiko Nishikawa group by X-ray diffraction discovered huge density fluctuations in supercritical fluids, which arise due to nanosized clusters and pores.

The knowledge of clusters’ and pores’ characteristics is vital for supercritical fluid based technology. The report demonstrates a new method of the fluids’ heterogeneity parameters extraction from the NIST Thermophysical Properties of Fluid Systems Database. This method, like a nanoscope, extracts bond energies of clusters and energy deficits in pores for subcritical and supercritical zones by computer processing of precise experimental thermophysical data.

Basing on the constant volume heat capacity $C_v$ and the internal energy $U$ of a pure fluid with a subcritical density, we estimate an averaged cluster bond energy $E_{cv}(T, D)$ in Kelvin by the expression:

$$E_{cv} = -T^2 \left. \frac{\partial C_v}{\partial U} \right|_T.$$ 

At a supercritical density this expression provides an estimation of the energy deficit in pores of a liquid-like fluid.

The report demonstrates the averaged energetic parameters for clusters and pores in a number of pure atomic, polar and non-polar molecular fluids. The density dependences of the $E_{cv}(T, D)$ clearly demonstrate the soft structural transition from gas-like to liquid like structures in supercritical fluids. The discovered symmetry between averaged cluster bond energies and energy deficits in pores shows a similarity of cluster structures in real gases with pores structures in dense fluids.
Temperature Control and Flow Manipulation for Nano-Confined Fluids
by Molecular Dynamics Simulations

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The control of temperature for molecularly structured fluids under flow conditions in molecular dynamics computer simulations is of critical importance for useful applications. As computational power continues to improve, the ability to perform simulations of very large and complex molecular systems is now feasible. The complexity of a system increases considerably when the system is both highly confined and under the application of an external field that drives fluid flow far from equilibrium. For such systems it has been demonstrated that thermostatting the fluid directly can induce simulation artefacts, and that the most reliable method is to thermostat only the confining walls, allowing heat to flow from the fluid into the walls as would typically happen in nature [1]. However, for complex wall structures, this can add an additional degree of difficulty, which can increase the required simulation time beyond feasible limits. In this presentation we propose a new method whereby instead of thermostatting the wall particles directly, we position vibrating “virtual” particles tethered to the walls that assume the role of a heat sink [2]. These particles do not interact with the walls and can pass straight through them. They do however interact with fluid atoms, thereby exchanging both energy and momentum. The new thermostat is compared to systems of thermostatted walls and shown to be reliable and efficient, without the introduction of unwanted artefacts. We use the new method to simulate the flow of water confined to physically realistic asymmetric planar walls composed of hydrophobic graphene and hydrophilic silica and thereby show that by spinning water molecules by the application of a rotating electric field we can induce unidirectional flow with only moderate temperature rise in the fluid [3].

References

A Study on the Energy Balance within a Bubble Column Evaporator

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A bubble column evaporator (BCE) system was used to determine accurate and precise enthalpy of vaporization ($\Delta H_{vap}$) values for concentrated salt solutions. The method is based on the steady state energy balance developed in a bubble column evaporator. The BCE system offers a novel and simple approach for $\Delta H_{vap}$ measurements because it only requires measurement of the hydrostatic differential pressure across the column and the temperatures of the steady state column solution and the inlet gas. BCE systems also have been studied and developed for many other applications, such as thermal desalination, sterilization and evaporative cooling. The energy balance and utilization involved in these processes form the fundamental theory for BCE applications. In this work, besides precise determination of $\Delta H_{vap}$ values, a comparison has been made between the originally proposed energy balance equation and a new energy balance equation. Experimental measurements obtained at low and high inlet air temperature were used to calculate the corresponding $\Delta H_{vap}$ values. At low temperatures of inlet air (~333 K), the new equation gave the same level of error percent compared with literature $\Delta H_{vap}$ values; while for high inlet air temperatures (423-548 K) the closest $\Delta H_{vap}$ values were given by the original equation. Typical energy consumption levels for thermal desalination for producing pure water using the BCE process was also analyzed with different inlet air temperatures.
We report on the use of a microsecond heat pulse by a fine wire to nucleate a vapor phase in a multicomponent liquid mixture. We have previously reported on the use of this thermally excited wire to overcome the nucleation barrier when detecting the boiling line. Morphologies resulting from this heat pulse depend upon factors such as the duration of the heat pulse, the total energy applied per pulse, the difference between the sample pressure and that of the equilibrium bubble point pressure, and the fluid composition. Measurements on synthetically prepared alkane mixtures as well as live reservoir crude oils will be presented.
The unique properties of ionic liquids (ILs), such as a negligible vapour pressure, high chemical and thermal stabilities, wide liquidus temperature range, and the possibility of fine tuning their properties through appropriate cation/anion combinations make of them viable candidates to replace the common organic and volatile solvents currently used in an extensive range of industrial applications [1]. In fact, there are circa 600 different organic solvents used by industry while there are one million of possible combinations of ions or different ionic liquids [1]. In particular, ionic liquids have been designated as potential solvents for “clean” liquid-liquid extractions [2]. Therefore, the search on novel biphasic systems composed of two ionic liquids, while comprising the determination of their liquid-liquid equilibrium, allows the creation of a new plethora of separation processes constituted only by non-volatile solvents. In this work, immiscible mixtures of cholinium- and phosphonium-based ionic liquids were investigated and their phase diagrams were determined from 40°C to 150°C. Nuclear Magnetic Resonance (NMR) and Electrospray Ionisation - Mass Spectrometry (ESI-MS) were used as analytical techniques for the quantification of each ion/ionic liquid and for the evaluation of the ionic exchange extension in such mixtures.

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References

Can correlation effects in a fluid confined in big but finite compartments linked by small openings, such as shallow channels, occur over distances much larger than the bulk correlation length? Recently, Gasparini and co-workers [1] have demonstrated such rather striking “action-at-a-distance” effects in a two-dimensional array of microscopic boxes filled with superfluid 4He and linked by either channels or a uniform film. The measurements of several responses show that under certain conditions these boxes can be strongly coupled. What seems to be crucial in this work is the size of boxes and connectors and the vicinity of the critical point. Perron and Gasparini [2] suggested that observed action-at-a-distance effects might be a more general feature of systems with phase transitions than is usually supposed. We present a system exhibiting extraordinarily long-range cooperative effects, on a length scale far exceeding the bulk correlation length. We give a theoretical explanation of these phenomena based on the mesoscopic picture of phase coexistence in finite systems, which is confirmed by Monte Carlo simulation studies. Our work demonstrates that such action-at-a-distance can occur in classical systems involving simple or complex fluids, such as colloid-polymer mixtures, or ferromagnets which can be confirmed experimentally.

References

It is shown how non-equilibrium thermodynamics can be used to describe energy conversion in electrochemical cells [1]. The entropy production is actively used to find the electric potential profile under reversible conditions and to define the overpotential. Two variable sets are useful, and we give the transformations between these. We next prescribe procedures for calculations of profiles of temperature, concentrations and electric potential across a cell. Applications to saline power plants and thermoelectric generators are briefly discussed.

References

The peculiarities of many materials during heating at the wide temperature range are chemical, phase and structural transformations accompanied by latent heat effects. The main problems in investigation of thermal physical properties of these materials can be formulated as follows:

- How to measure apparent thermophysical properties during chemical, phase and structural transformations;
- How to determine true thermal physical properties required for heat and mass transfer calculations during chemical, phase and structural transformations.

The problem in experimental measurements of thermophysical properties is the impossibility of using steady state methods during time-dependent physical and chemical processes in the materials. Using of transient methods, for example hot wire or laser flash methods, is also incorrect, since the measurement process has to be started only after steady state temperature field is established in the sample, i.e. when the processes could be finished. The best way to measure thermal physical properties during the processes is measuring during monotonic heating which can be a model of real technology. These methods are applied widely for test of specific heat based on DSC analyses. The special standard ASTM E2584 was developed for apparent thermal conductivity measuring during monotonous heating/cooling. We discuss in this paper some limitation of the standard methods and describe novel methods and technique for measurement of thermal diffusivity, thermal conductivity, and specific heat during monotonous heating of the sample. Determination of true thermal physical properties is based on excluding of latent heat effects and modeling of apparent thermal conductivity and heat transfer mechanisms. Thermal diffusivity and specific heat of materials with different composition and density (ceramics, gypsum, and minerals) were measured in this work in the temperature up to 1700°C. True thermal conductivity was determined as a product of the measured thermal diffusivity, volume specific heat in which latent heat effect were excluded.
New Method for Enlarging the Measuring Range of the Pulse-Echo Technique for Supercritical States

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Speed of sound data play an important role for the development and parameterization of equations of state for fluids. One method for the measurement of the speed of sound in fluids is the pulse-echo technique, where the propagation time of an acoustic wave burst in a fluid over a known propagation distance is determined [1]. This method is limited by the sampling of received echoes of the acoustic wave bursts, depending on damping due to acoustic impedance and attenuation effects. Improving this sampling by signal enhancement, applying a Fast Fourier Transformation on acoustic wave echoes, increases the signal-to-noise ratio and enhances the time and amplitude resolution. Additional pulse design leads to technical advantages for determining the propagation time also for highly distorted echoes due to the conditioning of the waveform of the echo. It is shown that this newly devised evaluation process significantly enlarges the measuring range of the pulse-echo technique in supercritical states.

References

It is demonstrated that interactions between nanoparticles and topological defects induce a twist-grain boundary phase in chiral liquid crystals [1,2]. The occurrence of this phase, the analogue of the Shubnikov phase in type-II superconductors, is driven by direct interactions between surface-functionalized CdSe quantum dots and screw dislocations. It is shown that, within an adaptive-defect-core-targeting mechanism, nanoparticles of appropriate size and functionalization adapt to qualitatively different cores of topological defects such as disclination lines and screw dislocations. This mechanism enables the effective reduction of the energetically costly, singular defect core volume, while the surrounding phase ordering remains relatively weakly affected. The findings suggest new pathways towards the controlled assembly of superstructures in diverse, symmetry-broken, condensed-matter systems, ranging from nanoparticle-decorated liquid crystals to superconductors.

References

Empirical Fundamental Equations of State Correlations Based on Hybrid Datasets

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The process engineering industry is in an ever increasing demand for thermodynamic data that cannot be satisfied exclusively with experimental measurements due to cost and time inefficiency. Moreover, often extreme thermodynamic conditions or hazardous fluids have to be considered. The primary purpose of empirical fundamental equation of state correlations (FEOS) is to extend the range of available experimental data by offering interpolation and extrapolation capability. A FEOS can be expressed in forms of various thermodynamic potentials. A thermodynamic potential has ability that every other thermodynamic property can be obtained as a combination of its derivatives with respect to its natural variables. The construction of a FEOS requires less data than the amount that would be needed to map the entire fluid region of technological relevance. Nonetheless, FEOS exist only for a very limited subset of the pure compounds that are in technological use. For mixtures, where the range of required data increases drastically with the number of components, the situation is much worse. Molecular simulation has evolved to a point where it can contribute effectively to thermodynamic data retrieval. Its predictive capability is limited only by the molecular interaction model that represents the investigated substance, molecular simulation can straightforwardly target any state point of interest while the associated financial cost and time requirement is only a fraction than that of a corresponding laboratory measurement. Besides the usual thermodynamic properties obtained from measurements, molecular simulation can directly deliver the derivatives of the FEOS with respect to its natural variables, making fitting procedures simpler.
Molecular Simulation Studies on HFO Based Working Fluids

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Due to their low Global warming potential (GWP) different hydrofluoroolefins are currently discussed as working fluids for various applications, either as pure compounds or as components in blends. Though, studies on the performance of these new working fluids in technical applications require information on various properties such as phase equilibria, transport and caloric properties over a wide range of state points. On the 18th Symposium on Thermophysical properties in 2012, we have presented a transferable force field for fluorinated propenes [1, 2] that enables reliable predictions for the thermophysical properties of this new class of refrigerants and their mixtures by molecular simulation studies. This force field has also been applied to yield predictions on the VLE and liquid phase properties of mixtures of fluoropropenes such as HFO-1234yf, HFO-1234ze with other working fluids like R-32 or CO2, and for the refrigerant blend R-445A [3-5]. The force field model has now been extended to include chlorinated components such as HCFO-1233zd or fluorinated butenes such as HFO-1336mzz. Thus, we will present molecular simulation results for the thermophysical properties of different HFO compounds, and also of their mixtures with other working fluids. Our simulation studies comprise Gibbs Ensemble Monte Carlo simulations on the vapor-liquid equilibria, and molecular dynamics simulations on liquid phase properties such as densities or viscosities. We will thereby present simulation results for different compounds and blends that are currently proposed as working fluids for technical applications such as mobile air conditioning systems, heat pumps and ORC processes.

References

Modeling of Thermodynamic Properties for Pure Refrigerants and Refrigerant Mixtures by Using the Helmholtz Equation of State and Cubic Spline Curve Fitting Method

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When simulating refrigeration systems or equipment, knowledge of refrigerant thermodynamic properties is required. While some of the refrigerants are made of pure fluids, some of these refrigerants are made by mixing of two or more pure refrigerants with a predetermined percentages. In modern trade and science, it is compulsory to get the same results in everywhere for the same inputs or measurements. Properties of refrigerants are a major part of international trade, therefore, it is a subject of interest of international standards. International Standard Organization (ISO) was prepared a standard for calculating real gas equation of states, for pure fluids and mixtures. The standard name is ISO 17584:2005(E). In the standard, Equations of States were given in Helmholtz free energy form. In this study a computer model was developed based on ISO 17584 equation of state and cubic spline curve fitting models developed by using saturation thermophysical properties of the refrigerants and refrigerant mixtures. Java programming language was used to model equation of state. As an example the equations for R1234yf and R410A were presented in this paper. With the new model, thermodynamic properties of R1234yf and R410A were compared with REFPROP 9.0. It shows that the total mean deviations of the new model are less than 0.5%.
Flake Thermal Conductivity of Graphene

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The Kubo formula for the thermal conductivity of per stratum of few-layer graphene, up to five, are analytically calculated within the tight-binding Hamiltonian model and Green’s function technique, compared with the single layer one. The results show that by increasing the layers of the graphene, this conductivity decreases. Although, the change in its magnitude varies less as the layer number increases to beyond two. This could be explained by overlapping of the normal oriented non-hybridized pz orbital. So that in analogy with isolated single layer, these inter-layer interactions provide new vertical channels for moving electrons and distract a fraction of their motivation from horizontal traces parallel to the layers, towards new built-in perpendicular tracks. In other words, overlapped non-hybridized pz orbital gives rise to a partial deviation of the electrons’ mobility from the planes for the sake of upright directions. The consequence of these inter-layer possibilities of movement would be a reduction in the intra-layer displacements, and hence, a decay in the flake thermal conductivity. This phenomenon is of more significance as the number of the layers increases, rationally compatible with the last argument, because adding more layers generates more detour paths for electrons, so the plane components of motion will bear a decline.
Ceramic materials are usually applied to the modern industry, especially in high temperature conditions, such as space shuttle, thermal barrier coating, and selective emitter for thermophotovoltaic systems. Understanding and controlling the spectral emissivity of the ceramic materials at high temperatures is indispensable in thermal design related with these applications. The spectral emissivity measurement method is presented on the base of the definition of the emissivity. An experimental setup for the measurements of the normal spectral emissivity of solid material at elevated temperatures is developed. The experimental setup covers the temperature range from 800°C and 1600°C and wavelengths from 1μm to 25μm. Sample is heated by a torch flame, and the sample surface temperature is determined by the Christiansen wavelength method. Two different temperature-tunable blackbody sources are used as the standard references and the radiance is measured by a FTIR spectrometer. Firstly, the validation of the Christiansen wavelength method is verified experimentally below 400°C with the comparison of the temperature results between a K-type thermocouple and Christiansen wavelength method, and the relative deviation is less than 2%. Next, the spectral emissivity of MgO at ambient temperature is measured to determine the Christiansen wavelength, and the measurement results of the normal spectral emissivity of MgO between 832°C and 1508°C are also presented. The results show that the Christiansen wavelength of MgO is found to be 12.5μm at room temperature and about 12.8μm at elevated temperatures. The spectral emissivity is influenced slightly by the sample temperature, and the absorption peaks around 3μm and 7μm at room temperature, which is caused by water, disappear at high temperatures. Finally, a thorough analysis of the uncertainty components of the emissivity measurement is carried out and the combined relative uncertainty of MgO sample at 1323°C is less than 4%.
Transport properties of transformer oil are important parameters for electric equipment designing. In this work, specific heat capacity of transformer oil was measured from 253K to 353K using flow calorimetry. At the same time, the influence of the transformer oil’s specific heat capacity was investigated. The specific heat capacity of transformer oil increases linearly with increasing temperature. Above all, the specific heat capacity of transformer oil is seldom influenced by refining depth and additives, while mainly affected by hydrocarbon composition. Different hydrocarbons have different effects on the specific heat capacity, and the order is alkanes; hydrocarbon composition; specific heat capacity; viscosity; flow calorimetry.
The nonequilibrium electrons and holes non-uniformly distributed arise in a bipolar semiconductor near its contacts with a metal when an electrical current flows through it. It causes non-uniform recombination, which creates nonuniform dissipation of heat [1] due to which the non-uniformly distributed temperature gradient arise [2]. It generates the thermal electrical currents, which together with the diffusion currents change the electrical conductivity of a semiconductor. It is shown that this electrical conductivity depends particularly on the thermal conductivity. It is shown that the electrical conductivity of a bipolar semiconductor of any lengths is equal to the sum of the electrical conductivities of electrons and holes only in the case of infinitely strong surface recombination on the contacts of the semiconductor with the metal. The partial cases are considered: the semiconductor with the large value of the thermal conductivity; the monopolar electron semiconductor; the monopolar hole semiconductor; the infinitely weak and strong values of the surface recombination rate; the different lengths of a semiconductor with respect to the generalized diffusion length, which depends on the thermal conductivity and the characteristic length, which characterizes the surface recombination rate. The concrete expressions of the electrical conductivity are obtained in all partial cases. The criterion of utilization of isothermal approximation (the temperature has its equilibrium value) for the calculation of a resistance of a semiconductor, which consists in that the thermal conductivity of a semiconductor must be sufficiently large, is established.

References

Compressed Liquid Density and Vapor Phase $PvT$ Measurements of cis-1,2,3,3,3-Pentafluoroprop-1-ene (R1225ye(Z))

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Cis-1,2,3,3,3-Pentafluoroprop-1-ene (R1225ye(Z)) is a non-flammable potential working fluid possessing low global warming potential. Toxicity testing has uncovered some concerns with sub-chronic and chronic exposures. In this paper, (1) liquid density data for eight isotherms from near saturation pressure to 35 MPa are presented, and (2) vapor phase $PvT$ data are presented. (1) The liquid density data are regressed using a Tait correlation, and (2) the vapor phase $PvT$ data are regressed using a Martin-Hou equation of state.
Helmholtz Energy and Extended Corresponding Models for Non-Polar Fluids and Natural Gases

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This work presents an overview of the results obtained with Helmholtz energy and extended corresponding (ECS) models for non-polar fluids, mixtures of those fluids and natural gas and related systems. In the proposed model, the mixture Helmholtz energy is represented by a term from an ECS model plus a correction term. The ECS term is based on temperature- and density-dependent shape factors relative to the Setzmann-Wagner reference equation of state for methane and the correction term is a mixing rule, in terms of local compositions, depending on reduced temperature and density; with the local compositions calculated by a coordination number model for square-well fluids. The model was applied to 18 non-polar fluids; 46 binary, ternary and quaternary mixtures of those components and 388 distinct-composition samples of natural gases. The model was tested against a total amount slightly exceeding 91,000 data and representative results, in terms of overall percentage average absolute deviations, were: for pure fluids: 0.175 in densities, 0.279 in vapour pressures and 0.638 in speeds of sound; for binary mixtures: 0.169 in densities, 1.233 in bubble-point vapour pressures and 0.108 in speeds of sound; and for natural gases: 0.060 in densities of pipeline-quality gases, 0.099 in densities of unusual-composition samples, 0.249 in densities of rich natural gases, 0.146 in saturated-liquid densities of liquefied natural gases and 0.220 in speeds of sound. Compared to the equations of state for technical applications, these results are satisfactory and allow concluding that the proposed models are alternatives in the context of technical applications.
This work presents an overview of the results obtained with Helmholtz energy and extended corresponding (ECS) models for refrigerants and mixtures of refrigerants. In the proposed model, the mixture Helmholtz energy is represented by a term from an ECS model plus a correction term. The ECS term is based on temperature- and density-dependent shape factors relative to the Tillner-Roth and Yokozeki reference equation of state for R-32 and the correction term is a temperature- and density-dependent mixing rule. The model was applied to 19 refrigerants of the methane, ethane and propane series and to mixtures of R-32, R-125, R-134a, R-143a, and R-152a. The model was tested against a total amount slightly exceeding 130,000 data and representative results, in terms of overall percentage average absolute deviations, were: for pure fluids: 0.187 in densities, 0.229 in vapour pressures and 0.662 in speeds of sound; for binary mixtures: 0.347 in densities, 0.467 in bubble-point vapour pressures and 0.077 in speeds of sound. Compared to the equations of state for technical applications, these results are satisfactory and allow concluding that the proposed model is an alternative in the context of technical applications.
Latent Thermal Energy Storage (LTES) systems in buildings and buildings envelopes have received serious attention for reducing energy use in building sector. Here, PCMs (Phase Change Materials) that absorb or release the energy equivalent to their latent heat when the temperature of the material undergoes or overpasses the phase change temperature can be effectively applied. The application of PCMs in thermal energy storage has been well known in many fields, such as in solar energy storage, waste heat recovery, and smart air conditioning in buildings. However, PCMs can be incorporated in wallboards, concrete, plaster, roof, underfloor and insulation of buildings in dependence on their properties, encapsulation etc. The effectiveness and usability of particular PCM material for specific part of building envelope must be experimentally verified case by case, in order to develop material having optimal thermophysical properties that allow moderation of interior climate temperature on desired value in dependence on changes of exterior conditions of building. Here, especially suitable phase change temperature, large latent heat and large specific heat of PCMs must be considered. Five different types of commercially produced PCMs are experimentally studied in the paper in order to find proper materials for incorporation in lightweight plaster composition. Within the DSC analysis, the researched materials are exposed to the temperature loading from -10°C to 60°C, with temperature change rate of 1, 5, 10, and 20°C/min. On the basis of DSC tests, temperature of phase change and heats of fusion and crystallization are accessed. The obtained data gives clear evidence of the effect of heating and cooling mode on materials performance, because of significant shift of DSC curves measured for similar material. This effect is closely discussed and evaluated, and the proper materials for application in light weight plasters are identified.
Physical Limit Stability in Supercooled Water

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Study of the curved interfaces is an urgent problem of the first-order phase transitions. Kiselev and Ely developed a general, based on the fluctuation theory of homogeneous nucleation, approach for the calculation of kinetic spinodal of liquids. The kinetic spinodal is defined by them as a locus, where the mean time of a formation of a critical nucleus becomes shorter than a characteristic time needed to decay fluctuations to the local equilibrium. The kinetic spinodal in their theory can be completely determined by the surface tension and the equation of a state of the metastable fluid. They discussed also the kinetic boundary for supercooled water. We will use our parametric crossover model for supercooled water and our measurements of the surface tension in supercooled region of water, and also the different models of the size dependence of the surface tension, to recalculate the kinetic spinodal for supercooled water. We will compare the calculated values with the ones calculated by Kiselev and Ely, and with the homogeneous nucleation curve presented by Holten et al., and with experimental data. Different models of the size dependency of the surface tension and their influence on the calculated spinodal curves will be discussed. One of the issues of the recent parametric equation of state of water is that the actual location of the hypothesized critical point is uncertain. We will discuss the problems connected with the uncertainty.
Fluctuation-Induced Pressures in Fluids in Non-Equilibrium Steady States

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Theory and experiments have shown that thermal fluctuations in fluids in non-equilibrium steady states are always long range encompassing the entire system. These fluctuations are strongly affected by finite-size effects and will induce non-equilibrium fluctuation-induced Casimir-like pressures. Specifically, we shall consider non-equilibrium pressures induced by temperature fluctuations in fluids in the presence of a temperature gradient and non-equilibrium pressures induced by concentration fluctuations in mixtures in the presence of a concentration gradient.
Capture or reduction of greenhouse gases emission to atmosphere is a very actual question at the present time. These activities depend on the processes between the rates of emission of the greenhouse gases into the atmosphere and the rates of processes that will remove or reduction it from the atmosphere. One of the most important greenhouse gases is carbon dioxide (CO₂), beside water. Emission of CO₂ to atmosphere is the main ecological problem, which increase of Earth surface temperature. CO₂ is scattering between the atmosphere and Earth surface, ocean through processes such as atmosphere-ocean gas transfer and chemical and biological processes. There are various technical processes, which are using for the capture of CO₂. One of these ways is solve of CO₂ into the liquids. Ionic liquids (ILs) are regarded as environmentally - benign solvents due to their very low vapor pressure and can be applied for helping with this CO₂ problem. The prediction of CO₂ solubility in ILs is a fundamental step toward the development of simulation tools to aid in the process calculations prior to industrial applications. The experiments to determine the high pressure solubility of CO₂ in tetrafluoroborate IL’s at various temperatures at T=(273.15 to 413.15) K are performed in a stainless steel measuring cell in equilibrium by using the isochoric method. Experiments were carried out in four different pressure steps: in the first step, the maximum possible pressure (about 5 MPa) is created in the gas reservoir. The other steps with maximum pressure are: second - about 3 MPa, third – about 1.5 MPa, and finally – about 0.5 MPa. The temperature dependency of Henry’s law constant was calculated. Thermodynamic properties of solution such as the free energy of solvation Δ_{sol}G, enthalpy of solvation Δ_{sol}H, entropy of solvation Δ_{sol}S and heat capacity of solvation Δ_{sol}C_{p} were calculated at various temperatures T to evaluate the solute-solvent molecular interactions. The measured CO₂ solubility in IL as a function of temperature and pressure are fitted to a virial equation using mole fraction dependence.
Ionic liquids (ILs) have been considered a dreamlike chemical due their unique properties, allowing a large variety of applications in all areas of the chemical industries. Diverse combinations of cation and anion lead to different physical properties of ILs. It is estimated that there are about one million possible of pure ILs. It should, however, be highlighted that the hydrophobic ILs are far outnumbered by the hydrophilic ILs, even if that class of ILs have been shown to be promising media for the extraction of compounds from aqueous solution. In this work, we report for first time the synthesis and key physical properties – density, viscosity, surface tension, refractive index, and water solubility – of novel hydrophobic ILs containing the perfluoro-tert-butoxide anion, ([Pftb]) as function of temperature and at 0.1 MPa, and compared them with those of other ILs with fluorinated anions. Systematic variation in the cation counterpart demonstrates how the physical properties of these ILs can be readily controlled. The Gardas and Coutinho group contribution methods were applied to the description of the pure component properties allowing the estimation of new group contribution parameters, to extend the applicability of these methods to new ILs. From temperature dependence of the measured properties, additional properties, such as isobaric thermal expansion, the surface entropy and enthalpy, and the critical temperature, were further estimated.
Ionic liquids (ILs) have been foreseen as alternative solvents to replace volatile solvent used in the current chemical and separation process. They are often known as designer solvents but their designer solvent character can be further enhanced by the use mixtures instead of pure compounds.

In the present work, we have studied the non ideality of ionic liquid mixtures in aqueous solutions as a method to develop heuristics allowing the design ILs formulation by mixing two ILs with different basicity, namely [C₄C₁im]Cl (high basicity) and [C₄C₂im][CF₃SO₃] (low basicity). The results here reported show that while the water activity of these mixtures cannot be considered a linear combination of the behaviors of the two binaries they cover nevertheless a wide range of basicities and that behaviour can be adjusted by the proper combination of two ILs in aqueous solution. This suggests the possible use of mixtures of variable basicity as alternative to the utilization of individual ILs in the design and optimization of advanced media for separations or chemical processing.
In the present manuscript, the advantages of surfactant micelles as vehicle are taken into consideration and the impact of potential antimicrobial drug (levofloxacin) on micellar system of anionic surfactant (SDS) has been studied. It would therefore be interesting to evaluate the region of micelle formation in order to design such system which could prove valuable in pharmaceutical formulations. For this, from conductance study, critical micelle concentration (CMC), standard thermodynamic parameters of micellization namely, and have been evaluated at four different temperatures (298.15 to 313.15) K. Molar volume and compressibility measurements have also been carried out to evaluate the apparent molar volume and apparent molar adiabatic compression of drug–surfactant complex and discussed in terms of the solute–solute and solute–solvent interactions. In addition spectroscopic analysis (FTIR and $^1$H–NMR) has also been carried out which confirmed the presence of intermolecular interaction present between levofloxacin–SDS moiety and provide information regarding locus of levofloxacin in micellar structure. Conclusively, this study provides a hint to assess and develop surfactant immobilized levofloxacin for better biological action.
Existing textbook expressions for the energy and heat capacity of gases and solids are widely taught in physics courses. However, no such expression exists for a liquid. The reason for this was summarized by Landau as "liquids have no small parameter", and discussed in some detail in Landau & Lifshitz Statistical Physics textbook. Based on the old idea of J Frenkel, I formulate the problem in the language of phonons, and calculate liquid energy and heat capacity for both classical and quantum cases. The resulting equation relates liquid heat capacity to its relaxation time with no fitting parameters, and is consistent with the experimental data of metallic, noble, molecular and network liquids [1]. The data includes several supercritical fluids from the NIST database. I subsequently discuss how thermodynamic properties of the liquid change above the critical point using the recent idea that the mean-free path defines the minimal wavelength of longitudinal phonons in the system and our recent finding of the crossover of liquid specific heat in the supercritical state [2]. I finally discuss the new Frenkel line recently proposed to exist in the supercritical state of matter [3]. Contrary to the existing view, we have shown that the supercritical state is not physically homogeneous in terms of physical properties, but exists in two distinct states: “rigid” liquids and “non-rigid” gas-like fluids separated by a dynamic transition across the Frenkel line on the phase diagram. All major properties of the system, including diffusion, viscosity, thermal conductivity, speed of sound and heat capacity as well as structure all undergo qualitative changes at the Frenkel line, from the liquid-like to gas-like [3,4].

References:

Adsorption of Mixtures of Yukawa Fluids on Solid Surfaces

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As precursors to the electric double layers, we examine the adsorption of Yukawa fluids on two types of planar walls: (a) hard walls and (b) Yukawa walls. The first type (hard walls) is for the purpose of establishing the baseline; the second type is to mimic the “electric double layers” of an “electrode/electrolyte” interface, since the Yukawa potential tends to the Coulomb interaction when the decay parameter approaches zero.

Type (I) System:
• Bulk Fluid: (attractive Yukawa interaction)
• Wall: Hard wall.

Type (II) System:
• Bulk Fluid: equal molar mixtures of species A and B molecules. A-A and B-B pairs interact via the repulsive Yukawa potential; while the A-B pairs via the attractive Yukawa potential.
• Wall: interacting with the “ions” via: \( w_{i,ext}(x)/kT = w_{HW} - 2\pi M Z_i x \).
  \( w_{HW} \) is the external hard-wall potential. The wall strength parameter (M) will be varied to simulate different degrees of charging via the surface charge density.

Monte Carlo simulations are carried out at temperatures from \( T^* = kT/\varepsilon = 0.76 \) to 1.25, and densities \( \rho^* = \rho \sigma^3 = 0.4, 0.7, \) and 0.8. Type I wall exhibits “depletion” at the two low densities, and “enhancement” at the highest density. Type II walls show more complicated behavior. The quantitative relation is modeled by a newly developed closure-based density functional theory with an OZ3-type bridge function.* We delineate the behavior by exhibiting the underlying singlet density, the cavity distribution function, and the chemical potential behavior that give rise to the observed phenomena. Implications on the electric double layers as found on the electrodes in the electrochemistry are explored.

References

Thermal Lens or the wavefront distortion induced by thermal lensing is a key effect in laser engineering and photothermal spectroscopy. The description of wavefront distortion induced by laser absorption in optical elements is fundamental in the design and evaluation of solid state lasers, optical windows and other passive optical components for high power laser systems. In addition, monitoring the dynamic process of optical path difference (OPD) with photothermal methods enables direct quantitative access to many physical properties of a large class of materials. The amplitude of the thermal lensing or its dioptric power is proportional to the OPD between the center and border of the beam, which is proportional to the heat power. This distortion is a result of complex photoelastic effects that characterize the degradation and the propagation of the beam. Due to thermally induced mechanical stress and bulging of end faces of the sample, OPD depends critically on the geometry of the sample. Simple analytical solution is obtained only for low absorbing materials, with the assumptions that the stresses obey either thin-disk or long-rod type distributions. In this investigation, TL measurements were performed as a function of the sample length keeping the same heat power. It is experimentally demonstrated that for materials with positive temperature coefficient of the refractive index the OPD increases typically 30 to 50 % with the decrease of sample length (from long rod to thin-disk geometry). For materials with negative temperature coefficient of the refractive index, this variation is much larger due to the cancelation of the different contributions to OPD with opposite signs. Furthermore, the experimental investigation presented here validates a recently proposed unified theoretical description of the TL effect, "J. Opt. Soc. Am. B 29, 3355 (2012)", which relates the OPD to the temperature profile in a relatively simple manner for all classes of absorbing optical materials. This generalized model could have significant impact on designing laser systems and has direct application in photothermal techniques in the determination of thermal, optical and mechanical properties of solid materials.
For the successful and reliable modeling, simulation, design and control of processes involve the polymeric materials, such as membrane fabrication from polymeric solutions, the thermo-physical properties such as PVT data, critical properties, solubility parameters, etc. are required. A number of advantageous outcomes were obtained through our investigations on determination of thermo-physical properties of polymeric systems as listed below, which were made possible by the introduction and application of a simple novel computational algorithm on intelligent coupling of molecular structure information, PVT data and equations of state.

# 1 - Modified group contribution method for accurate estimation of thermo-physical properties

# 2 - Molecular structure based method to define the PVT relationships in the form of Tait equation

# 3 - Algorithm to adapt any equation of state (EOS) for thermo-physical properties and phase calculation of polymeric systems, in particular cubic EOS

The research methodology involves these steps;

(i) The available literatures were reviewed to retrieve information on PVT data of polymeric systems in the form of tabulated data point, empirical models, theoretical models etc.

(ii) A well-established group contribution method was modified by introducing a chemical structure descriptors based function as results in # 1.

(iii) The data of steps (i) and (ii) were used to tailor a generic cubic equation of state as results in #3.

(iv) since the equations of state represent PVT data, by implementation of modified group contribution method (#2), the equations of states available in literatures were used to develop Tait model for (1) all systems of step (i) to check the EOS consistency and then (2) for other interested systems as results in #2.

The proposed algorithm and all aforementioned obtained results have been presented and discussed in details.
In recent years, ionic liquids (ILs) have shown to be able to form aqueous biphasic systems (ABS) in the presence of salts, amino acids, carbohydrates or polymers [1]. Furthermore, it has been shown that it is possible to tune the polarity and affinity of the coexisting phases in IL-based ABS by an adequate manipulation of the chemical structure of the IL ions [2]. Nevertheless, the polarity of the opposite IL-rich layer is always more restricted since it is usually composed of high charge density salts or of more hydrophobic polymers. In this context, the tailoring ability of IL-based ABS can be expanded by the combination of two ILs in aqueous media. In this work, novel ABS composed of two ILs were investigated. The binodal curves, and respective tie-lines, tie-line lengths and critical points were determined at 298 K. Several combinations of ILs, ranging from imidazolium-, phosphonium- and cholinium-based, were investigated. The partition coefficients of a series of dinitrophenylated (DNP) amino acids were also determined allowing to confirm the boost on the relative hydrophobicity of the coexisting phases achieved by IL-IL ABS. These novel liquid-liquid systems represent a relevant improvement on separation processes allowing thus for more specific and efficient extractions by the proper choice of the phase-forming components, which are ILs, of a given ABS.
This paper is intent to develop quantitative structure property relationships to estimate occupational exposure limits values. Occupational Exposure Limits (OELs) are representing the amount of a workplace health hazard that most workers can be exposed to without harming their health. There are different OELs such as threshold limit value (TLV of ACGIH), permissible exposure limit (PEL of OSHA), recommended exposure limit (REL of NIOSH) and maximum concentration value in the workplace. A new method for the estimation of properties of pure organic compounds is presented. The model is easy to implement and use.
Modeling the Dynamic Viscosity of Highly Polar Fluids Via the Use of Density Scaling

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Casalini and Roland [Phys. Rev. E 69, 062501 (2004); J. Non-Cryst. Solids 353, 3936 (2007)] have effectively proven that both the dielectric relaxation times and the viscosity of liquids can be graphically represented into a single master curve as a function of the thermodynamic potential \((T \rho^\gamma)\), where \(T\) is the temperature, \(\rho\) is the molar density, and \(\gamma\) is a state-independent scaling exponent. In this work, we applied the aforementioned thermodynamic scaling to the dynamic viscosity of highly polar and associating fluids such as water, alcohols, \(\text{H}_2\text{S}\), etc. Unlike previous studies on density scaling of transport properties, a more suitable normalization of the dynamic viscosity was used in this work in order to obtain improved correlations of viscosity over much wider temperature and pressure ranges encompassing the zero-density limit, the high-density region, the gas-liquid saturated line and the vicinity of the critical point. A calculation procedure is also described here to optimize the value of the scaling exponent \(\gamma\) that ensures the best superpositioning of all experimental isotherms considered.
In order to fully understand and model the flow of hydrocarbons in important oil and gas processes such as enhanced oil recovery and carbon capture and storage, reliable transport properties data of asymmetric fluid mixtures at high-temperature and high-pressure (HTHP) reservoir conditions are required. In this research, we have measured simultaneously the viscosity and density of the asymmetric binary mixtures of squalane with dissolve methane at different compositions under HTHP conditions. The measurements were conducted using a bespoke vibrating-wire viscometer-densimeter (VWVD) and have an estimated expanded uncertainty of 2% in viscosity and 0.2% in density. The measurements were made at a wide range of temperatures, (323.15 to 448.15) K, and at pressures up to 200 MPa. The VWVD device was operated in an absolute manner in relation to the determination of viscosities. To facilitate this mode of operations, the radius of the centreless-ground tungsten wire was measured accurately with a laser micrometer. In relation to the density measurements, a single point calibration was required and this was carried out in n-nonane at T = 298.15 K and p = 0.1 MPa. The density results have been correlated with a modified Tait [1] equation, whereas the viscosity results are compared with the predictions of the hard sphere model of Dymond and Assael [2, 3] within its range of validity. Once again the results show clearly that dissolution of methane in squalane leads to both a dramatic reduction in the viscosity and a small increase in the density of the latter.

References


Open Thermodynamic System Far from Equilibrium Increases Its Entropy During Growth!

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In the last hundred years several attempts have been made to develop a mathematic formalism able to describe life processes. Traditional models of aging predict that cells/organisms decrease their entropy during their life spans. Life, death, and after death decomposition are a part of same continual physical, chemical and biological process. This article attempts to develop a mathematic formalism that would be able to describe life processes, diseases, death process and after-death decomposition process. The new model proposed in this research includes four anabolic reactions, three self-assembly process, two metabolic error reactions, one catabolic reaction, ionic pump work, muscle work, and three decomposition reactions. The metabolic error reactions and decomposition processes included in this model can’t be found in other models in literature. An equation of cell entropy balance was derived. Analysis of the derived equation shows that entropy of a growing cell increases during its life span. This is in accordance with experimental results found in the literature. The chemical apparatus of a cell functions as two biological machines. Trough synthesis and self assembly reactions the first machine decreases the entropy imported with substances necessary for growth, but as any machine it is imperfect according to the second law of thermodynamics. The second biological machine responsible for reparation of metabolic errors and damages is also imperfect. The efficiency of any (including the biological) machinery is always less than 100%. Biological machine can’t completely compensate all the entropy imported with mass and errors. As a consequence of growth a change of volume, mass, amount of substance and accumulation of entropy appears which leads to change of thermodynamic state of the cell (and organism). The accumulation of entropy is also consequence of metabolic errors and degradation of complex molecules. The accumulation of entropy and therefore change in thermodynamic state of the organism is the physical basis of the aging process.
Our intuition suggests that life and death are two completely different and opposite processes. Some models predict that organisms decrease their entropy during life, and begin to increase it after death. The entropy increase was experimentally found to be one of the main characteristics of both life (through aging) and death. During life entropy increases and accumulates in organisms. During death process the entropy of the surroundings increases (caused by decomposition of the organisms). Biological cell or an organism can be considered as an open thermodynamic system far from equilibrium. Corollary, life is a physicochemical process. Actually, it will be shown that Life is the complexity of many mutually opposed processes. The physical state of each living system depends on balance of those processes. Normally, those processes are not fully balanced, so the biothermodynamic system continuously changes its state during life. The direction of change is dictated by increase of entropy. There are four main groups of processes: 1) Exchange of matter and energy with the surroundings; 2) self assembly processes, and metabolic errors; 3) decomposition processes; and the 4) reparation and regeneration processes. They are together – representation of the life itself. The dominance of the import and accumulation of substances (and therefore the growth), and self assembly processes as well as the reparation processes are the main characteristic of life. The dominance of decomposition is characteristic of death. The increase of entropy during time evolution of physical state of the cell/organism is experimentally confirmed ($dS_{cell}>0$), so the changes of the systems are inherent to life, and they are irreversible. The equations derived in this article clearly and certainly lead to conclusion that, sooner or later, the self-organizing chemical activity and reparation in the biothermodynamic system must cease. Consequently, termination of any living system is unavoidable. The termination of life is not simply the end of one simple process. However, the termination point could be delayed, so even if immortality is impossible, longevity is a quite affordable goal. The end is certain, but when it will be, that depends in a large extent on us.
Comparative Study of Entropy and Information Change in Closed and Open Thermodynamic Systems

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In this analysis we discuss the entropy and information aspects of closed and open thermodynamic systems. The information and entropy change of the system during processes of synthesis and decomposition are discussed in the context of RNA synthesis. The analysis suggests that during synthesis reactions in a closed thermodynamic system, its information content increases while its entropy decreases. In degradation reactions occurring in closed systems information decreases while entropy increases. In open thermodynamic systems performing synthesis reactions both entropy and information content increase. Entropy of an open thermodynamic system increases because of flux and accumulation of particles. Entropy increase is partly reduced by reactions of synthesis and self-assembly processes. In open systems performing decomposition processes both entropy and information content decrease. Entropy of an RNA molecule decreases during loss of nucleotides, because nucleotides leave the open system taking the entropy with them.
The Entropy Change in Open Thermodynamic Systems Far from Equilibrium in Self-Assembly Processes

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The dogmatic claim that cells as real life open thermodynamic systems decrease their entropy is almost 100 years old. The textbook literature and articles in the field of biochemistry, physical chemistry, and life sciences describes the changes of entropy of open thermodynamic systems (i.e. cells) in self organizing processes as negative. However, it was found experimentally that entropy of organisms actually increases over time. Our analysis of behavior of both, closed and open thermodynamic systems was made through modeling. It showed how entropy of open thermodynamic systems far from equilibrium in self organizing processes changes during growth (with addition of monomers). The analysis is extended to real life versions of open thermodynamic systems.
Casalini and Roland [Phys. Rev. E 69, 062501 (2004); J. Non-Cryst. Solids 353, 3936 (2007)] have effectively proved that both the dielectric relaxation times and the viscosity of liquids can be graphically represented into a single master curve as a function of the thermodynamic potential ($T \rho^{\gamma}$), where $T$ is the temperature, $\rho$ is the molar density, and $\gamma$ is a state-independent scaling exponent. In this work, we applied the aforementioned thermodynamic scaling to the thermal conductivity of saturated hydrocarbons from methane to $n$-decane. Unlike previous studies on density scaling of transport properties, a more suitable normalization of the thermal conductivity was used in this work in order to obtain improved correlations of thermal conductivity over much wider temperature and pressure ranges encompassing the zero-density limit, the high-density region, the gas-liquid saturation line and the vicinity of the critical point. A calculation procedure is also described here to optimize the value of the scaling exponent $\gamma$ that ensures the best superpositioning of all experimental isotherms considered.
Solubility of Carbon Monoxide in Different Bio-Oil Components

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The solubility of carbon monoxide has been determined in five different bio-oil components namely crotonaldehyde, diacetyl, methylfuran, allyl alcohol and furan at three different temperatures 273.15, 298.15 and 323.15 K and the pressure range from 1 to 7 MPa. The measurements were carried out using static analytic VLE (Vapor-liquid equilibrium) cell equipped with ROLSI™ (Rapid Online Sampler Injector) sampler connected to a gas chromatograph through a heated transfer line. PC-SAFT EOS was employed to model the acquired data. Pure component parameters of the PC-SAFT \((m,\epsilon,\sigma)\) of the bio-oil components were calculated by a simultaneous regression of vapor pressure and liquid molar volume data using Aspen Plus®. Binary Interaction parameters for PC-SAFT have also been regressed. Carbon monoxide solubility in all cases was found to be very low.
Numerical Investigation on the Fuel Spray Processing for the Mild Combustion

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Mild combustion is recently attracted attention of many researchers in the fields of combustion and internal combustion engines. The importance of the mild combustion is because of existing of low temperature flame in this kind of combustion and consequently less production of major pollutants like NOX and also increasing of the combustion efficiency. In this paper a numerical investigation is carried out for providing a fuel spray for the mild combustion. AVL FIRE software is used for the numerical simulation of the problem. The key idea in this research is providing a relatively strong vacuum region inside the fuel spray plume and consequently suction of more ambient air into the fuel spray which in turn provides a lean mixture of the fuel and air and decreases the temperature of the flame. Lean mixture of the fuel and air in conjunction with reduction of flame temperature provide proper conditions for the mild combustion of the fuel and consequently decrease the major pollutants like NOX and increase the combustion efficiency.
We are able to nucleate bubbles in single-phase fluids at high pressure using a brief thermal pulse through an immersed wire. Using high speed video, we observe in some fluids that bubbles are ejected radially from the wire at high speed (>10 cm/s) while in other fluids the bubbles remain affixed to the wire. Bubble ejection is attributed to thermal Marangoni forces arising from the large temperature gradient (> $10^7$ K/m) caused by the thermal pulse. In most fluids, surface tension decreases with increasing temperature, causing bubbles to remain near the hot wire. In certain mixtures, however, surface tension increases with increasing temperature causing bubbles to be driven away from the hot wire. Tests with binary alkane mixtures show good agreement between predicted surface tension variation and observed bubble behavior.
The electrocaloric effect (ECE) has attracted great interest for developing new cooling devices that have the potential to reach better efficiency than the existing cooling technologies [1,2]. Recently, it was shown that it can be exploited in studies of the electric field-temperature phase diagram of relaxor ferroelectrics [3] since the sharp ECE anomaly can be observed at the ferroelectric phase transitions [4,5]. Motivated by the long-standing unresolved enigma of the relaxor ferroelectric ground state, we performed a high-resolution electrocaloric, heat capacity and polarization study of the field-induced phase transition in the relaxor ferroelectric single crystal Pb(Mg1/3Nb2/3)O3 (PMN). We show that the discontinuous evolution of polarization as a function of the electric field or temperature is a consequence of a true first order transition from a glassy to ferroelectric state, which is accompanied by an excess heat capacity anomaly and released latent heat. We also find that in a zero field there is no ferroelectric phase transition in bulk PMN at any temperature, indicating that the nonergodic dipolar glass phase persists down to the lowest temperatures [3]. The high resolution electrocaloric measurements in the lead free BaTiO3 demonstrate that the highest electrocaloric response is achieved always at the temperature corresponding to the TC(E=0). A review of recent ECE findings obtained in perovskite relaxor materials including thick ceramic multilayers, substrate-free thick films and thin films will be given. Besides the recent advances in development of practical cooling devices utilizing different approaches and materials will be presented.

References

This paper is focused on the measurement of temperature dependence PCM. Transient methods were used to determine the thermal parameters: thermal diffusivity, thermal conductivity and specific heat. The method was applied to the selected PCM - derivatives of erythritol and mannitol. Interval for temperature dependency was chosen so that it is possible to study a macroscopic change in phase region (118 ° C, resp. 169 ° C). The gained knowledge will be used in the design of heat exchangers.
Transport Properties Driven by Short Range Order in Melts

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Structure-property relationship is a central issue of materials research. For liquid materials, however, it is difficult to understand how the internal structure influences their properties because it remains an experimental challenge to image the local arrangement of atoms in a disordered system. It is all the more crucial that it is now well accepted that a liquid is not a completely random disordered state but has generally the tendency to have a local structural order. This is particularly true for liquids such as Si and metallic liquids for which ab initio simulations provide direct evidence for the presence of local structural ordering and allow us to study the details of a such a structure and its lifetime [1-4]. Such a signature of local structural ordering is found to be more pronounced at lower temperatures, below the melting point $T_m$, in the undercooling regime. However it was also shown that this local structural order can exist even above $T_m$. Transport properties, like the shear viscosity and the diffusion coefficients are kinetic key parameters that determine the crystal nucleation and growth in materials. They also play a very important role in studying the liquid-to-glass transition in a glass-forming system. In experiment the determination of transport properties in the undercooled regime is rather challenging, because any contact of the melt with the container wall immediately induces crystallization of the melt. The convection inside the sample in terrestrial measurements is another problem. Very recently, we have shown that both the shear viscosity and the diffusion coefficients can be determined very accurately for Si and metallic melts using ab initio molecular dynamics [5-8] as well as the hydrogen diffusivity [9]. In this presentation, we will show how the local structural order influences dynamic properties of metallic melts and their evolution as a function of temperature. The relationship between structural and dynamic properties allow us to discuss liquid-solid transition like crystal nucleation and glass formation but also universal laws that relate transport properties to the excess entropy [10].

References

An Energy-Based Unit for the Thermodynamic Temperature

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Steps have been taken to define basic units in terms of fundamental constants, e.g. the kilogram is now to be based on an exact value of the Planck constant. In a similar way, it is possible to define an energy-based unit for the thermodynamic temperature by including known constants in the temperature itself:

\[ T' = \frac{1}{2} k_b N_A T = \frac{1}{2} R_{un} T \]

\( T' \) = consolidated thermodynamic temperature (J mol\(^{-1}\))

\( T \) = conventional thermodynamic temperature (K)

\( k_b \) = Boltzmann constant (1,380 650 5 *10\(^{-23}\) J K\(^{-1}\) )

\( N_A \) = Avogadro’s number (6,022 141 5 *10\(^{23}\) mol\(^{-1}\))

\( R_{un} \) = universal gas constant (8,314 472 7 J K\(^{-1}\) mol\(^{-1}\))

It is suggested that the unit J mol\(^{-1}\) should be given the name boltzmann, short form: Bo, because the Boltzmann constant will abrogated if the proposal is implemented. The introduction of the concept will have no impact on thermodynamic theory and present the same problems to thermometry as fixing the value of the Boltzmann constant has. The concept may be introduced without referring to either Boltzmann constant or kelvin:

“At the present state of thermometry, the thermodynamic temperature of the triple point of water, \( T'_{TPW} \), is 1 135, 590 XX J mol\(^{-1}\)”. \( (T_{TPW} = 273,16 \text{ K}) \) The thermodynamic temperature of a substance is the mean kinetic energy of particles per degree of freedom.

By introducing the Avogadro number into the definition, the numerical value is raised to everyday-life magnitude. The definition takes care of the temperature as integrating factor and as an intensive property of state. The molar entropy will be a pure number. In the Boltzmann equation that relates entropy to the probability of a state, the Boltzmann constant is replaced by 2/N\(_A\). The equation then contains pure numbers only, in line with Shannon’s information theory. Learning, teaching and applying thermodynamics will benefit from the lack of conversion factors (\( k_b \) and \( R_{un} \)). The proposal is intended to replace kelvin in thermodynamics, not Celsius or Fahrenheit in everyday life.
Thermal Conductivity of Nanofluids Containing Metal Oxide Nanoparticles

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Fluids contained nanometer sized particles exhibit much greater effective thermal conductivity than predicted by most of the developed relations. Interfacial layer might play a key role on the enhancement of effective thermal conductivity of nanofluids. Water based nanofluid samples were prepared containing metal oxide nanoparticles. Effective thermal conductivity of these samples has been measured by a laboratory made parallel wire technique as a function of weight fraction of filled metal oxide nanoparticles. A model which includes the effect of interfacial layer is proposed here. Besides interfacial layer some additional effects including concentration of nanoparticles, thickness of nanolayer and thermal conductivity of interfacial layer has also been accounted in this paper. Comparison with Maxwell and Renovated Maxwell model shows that our predictions are closer to the experimental results. Artificial Neural Network (ANN) architecture with 4-input and 1-output, in which one of the input is thickness of interfacial layer has also been utilised to predict effective thermal conductivity of nanofluids. Comparison indicates that ANN predictions are better than any other theoretical model.
Poly(2-hydroxyethyl methacrylate) (PHEMA), a synthetic crosslinked hydrogel, with outstanding ability to absorb and retain a high water content and still maintain their solid state, has been studied as scaffold for methane gas hydrates. The high water content, excellent hydrophilicity and interconnected pores of these hydrogels could be ideal to support the methane hydrate formation and to enhance gas permeation and interactions with water molecules. Supposedly, the heat released during the formation of 1 kg of methane hydrate is as much as 438.54±13.78 KJ. Whether the heat can be removed from the hydrate-hydrogel system in time is critical to the formation of methane gas hydrates, which is why high thermal conductivity, one of the thermophysical properties used to quantify the ability to conduct heat, is regarded as a favorable property. To better understand the thermal behavior of PHEMA hydrogel during the hydrate formation process, we investigate the thermal conductivity of PHEMA hydrogel under various temperatures ranging from 243 K to 293 K. Results were found that thermal conductivity is mainly influenced by 2 factors--ambient temperature and water content of hydrogel. At some point below 273 K, the thermal conductivity of all the hydrogels experiences a sudden rise to around 1.5 W/(m·K), about 3 times larger than before. We also found that the lower the water content is, the lower the transition point temperature will be. Additionally, we use TG and DSC together to investigate the water content and water state of hydrogels to better understand these hydrogels’ thermal behavior.
A thermoelectric energy converter is able to convert excess heat from various sources at various temperatures to electric energy. The efficiency of this conversion is low, and research has so far focused on the use of semiconductor materials. Seebeck coefficients of these materials amount to 0.3 mV/K. Theoretical descriptions of the thermoelectric cell [1] predict that molten salts (ionic liquids) and gas electrodes can increase this value several times. We report measurements of Seebeck coefficients for molten alkali carbonate mixtures with carbon dioxide and oxygen gas on gold or platinum electrodes, confirming a first study from 1977 of this cell [2]. Results are presented for pure (Li2CO3) and mixed carbonates (e.g. Li2CO3, K2CO3(l)) at stationary state, in the absence and presence of MgO(s) and in the temperature range 550 - 750 °C. Data are reduced according to the theory of non-equilibrium thermodynamics for heterogeneous systems. The total gas pressure was 1 bar. The composition of oxygen, carbon dioxide and helium were systematically varied and shown to confirm the theoretically expected stoichiometry of the electrode reaction. The Seebeck coefficient varied between 1.2 and 1.4 mV/K depending on the electrolyte composition; the highest values were typical for mixtures of alkaline carbonates. The temperature dependence of the coefficient was negligible, as expected at the high temperature used. The transported entropy of the carbonate ion of in pure molten Li2CO3 was calculated to 281 ± 3 J/mol.K, increasing to 297 ± 1 J/mol.K when the melt was saturated with MgO(s). This value is more than one order of magnitude larger than the transported entropy in a semiconductor. The data enable us to prescribe operating conditions for thermoelectric converters with higher Seebeck coefficients. This work supports the idea that the technology could benefit from systematic studies of complex-formers and gas reactions in the electrolyte.

References

Acid gases (mainly CO$_2$ and H$_2$S) are usually removed from gaseous streams by countercurrent contact with an aqueous amine solution. This is a consolidated industrial technology and is preferred to physical absorption because of the presence of the amine in the liquid phase, which undergoes to chemical reactions and so enhances the mass transfer. Due to the exothermicity of reactions, a temperature increase occurs in the absorber, affecting the equilibrium and the amount of absorbed acid gas, while in the regenerator the energy requirement at the reboiler strongly depends on the heat of desorption. A correct information on the enthalpy, then, is fundamental to design the acid gas removal section of an industrial plant, mainly in an energy saving perspective. The aim of the work is the analysis of the thermodynamics of the system composed of CO$_2$, water and methyldiethanolamine (MDEA), a tertiary amine widely used also if a separate removal of H$_2$S and of CO$_2$ is desired. The study is focused on the computation of the heat of absorption, which, in the open literature, is a field less investigated than the one related to VLE calculations. It is related to the description of the Vapor-Liquid Equilibrium, performed with the Electrolyte-NRTL model, and thus of the adopted VLE parameters. New parameters have been obtained and checked against experimental data of VLE and of heat of absorption. They can be implemented in the commercial software ASPEN Plus$^*$ and employed for simulations of the amine scrubbing scheme.
Fuel additives are used to accelerate combustion process, to improve combustion efficiency, and to reduce off gas pollution. DIPE and MTBE have been considered as two important additives in petrol. However, there is little experimental data concerning their thermophysical properties. The mutual diffusion coefficient is one of these properties and is related closely to the atomization and combustion process within combustion engines and is required for numerical simulation of the combustion process. But the data of mutual diffusion coefficients related to DIPE or MTBE is rare. So the prediction and measurement of mutual diffusion coefficient is of increasing interest. The digital holographic interferometry was employing. This method is one of the most widely used techniques with good accuracy for diffusivity studies of transparent liquid. A new method to determine the zero time of starting to diffuse was proposed in this work. Therefore, the problem presented by Szydlowska et al. (1982) that diffusion coefficient measured in one experiment became larger with time increasing was avoided obviously. The standard uncertainty in temperature is 0.016 K and the relative expanded uncertainty in mutual diffusion coefficient was estimated to be less than 1.5% over the whole investigated thermodynamic range. The accuracy of our apparatus is certified by measuring the mutual diffusion coefficient of KCl in water with the concentration of 0.33mol/L at 298.15 K. The absolute average deviation of experimental results with literature data is about 1.3%. 2,2,4-trimethylpentane(isooctane) was selected as the standard substances substituted for petrol because petrol is a complex mixture and isooctane has the similar combustion characteristic and carbon numbers with petrol. So the mutual diffusion coefficients of DIPE and MTBE in isooctane were measured at temperature ranging from 293.15 to 343.15K, respectively. Then the experiment data were correlated as the functions of temperature and concentration of DIPE and MTBE, respectively.
Research of Thermal Stability of Aliphatic Alcohols and Their Aqueous Mixtures

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The process of thermal decomposition of aliphatic alcohols (methanol, ethanol, 1-propanol and 1-butanol) and their aqueous mixtures in the range of temperatures 513.15 – 663.15 K was studied using the method of isothermal pressure increasing in a closed system. The starting temperatures \( T_H \) of thermal decomposition (decomposition points) of dissolved in water alcohols are obtained. Values of \( T_H \) depending on composition \( x \) and number of carbon atom \( C \) are described by the polynomial equation

\[
T(x,C) = 23.622x^2 - 65.617x + 6.378 \times 10^{-3} C^2 + 28.826 \times 10^{-2} + 544.258
\]

It is shown that values of \( T_H \) decrease with increasing of alcohol concentration and increase with increasing of carbon atom. The rate of thermal decomposition of alcohol molecules depending on temperature, number of carbon atoms and concentration in water is evaluated. The changes of thermal coefficients (isothermal coefficient of compressibility \( \kappa_T \), coefficient of cubical expansion \( \alpha \) and thermal coefficient of pressure \( \beta \)), and main thermodynamic properties (\( C_v \), \( C_p \), \( H \), \( S \), \( U \), \( F \), \( G \)) of studied mixtures depending on isothermal pressure increasing during the thermal decomposition of alcohols were calculated. To estimate rate of thermal decomposition of alcohols we used change of pressure of system in a unit of time at constant temperature and volume (closed system). Reaction rate constant was calculated by formula:

\[
k = \frac{1}{p} \frac{dp}{dt}
\]

where \( k \) – reaction rate constant; \( p \) – pressure; \( \tau \) – time; \( \frac{dp}{dt} \) – rate of reaction. Values of kinetic and activation parameters of alcohol decomposition in the range of temperatures 583.15 – 663.15 K are estimated.
Density, Surface Tension and Viscosity of Liquid SnZn Alloys with Na Addition

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In this work data for liquid SnZn alloys with Na addition are presented. The physicochemical properties, viscosity, density and surface tension, were measured using the discharge crucible method (DC) [1]. The experiments were conducted for Sn15Zn alloys with 0.1, 0.2, 0.5, 1.0, 3.0 and 5.0 % Na (at %). The measurements of properties of Sn15Zn+Na were performed over 548-823K temperature range. The results show that the addition of Na to Sn15Zn causes the decrease of density, surface tension and viscosity compared to eutectic SnZn alloy [2]. The obtained values of surface tension were compared with Butler model and with the Moelwyn-Huges, Sichena-Boygen-Seetharaman, Seetharaman-Sichen, Kozlov-Romanov-Petrov and Kaptay models for viscosity. The received a consistent physicochemical properties database for eutectic SnZn with Na additions.

References


Acknowledgments

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Analysis and Calculation of Thermodynamic Functions of Atoms and Organic Compounds of I-VII Groups of Mendeleev’s Periodic Table in Gaseous and Condensed Phases

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The values of free energies, the heats and entropies of formation of atoms of I-VI groups of Mendeleev’s periodic table in gaseous and condensed phases were analyzed. Seventy nine equations of such type as $\Delta_{c,f,s}^{o}Y= i \pm f N$, in which $\Delta_{c,f,s}^{o}Y$ is thermodynamic function, $i$ and $f$ are stoichiometric coefficients. The obtained equations can be used for the calculations of the same functions for other atoms, for which they are not known. The same equations can also be used for the next calculation of bond strength. Instead of bond energy ($E_b$) or bond dissociation energy (BDE) the bond strength ($S_b$) new symbol of the bond powers for organic and organometallic substances has been suggested. It has been done because there are all thermodynamic functions for practically all atoms of Periodic table and hard to define the bond power with the use the heat function (enthalpy) only; probably is necessary to present the all thermodynamic parameters for the calculating bonds between atoms [1]. The heat of vaporization ($\Delta_{vap}^0 H$), all thermodynamic functions $\Delta_{c,f}^0 G$, $\Delta_{c,f}^0 H$, $S^0$, $\Delta_{s}S_{cond}^0$ and heat capacity ($C_p$) of organic compounds of I-VII groups of Mendeleev’s Periodic table can be well characterized with the number of valence electrons $N$ without taking into account the number ($h$) of lone electrons pairs ($g$) of them in equation $\Delta_{vap,c,f,s}^0 \Psi^0 = i \pm f \ast (N - hg)$. The stoichiometric coefficients $i$ and $f$ reflect partially a various spatial structure of all investigated compounds. The free energy and entropy of combustion and formation are calculated only for oxygen, sulfur and partly fluorine compounds [2, 3].

References

Combining Fast-Scan Chip-Calorimeter with Molecular Simulations to Study Polymer Crystal Melting

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Recent development of fast-scan chip-calorimeter techniques allows us to expand the time window of our Differential Scanning Calorimetry measurements on polymer crystal melting towards the mini-second scale, and to match with our high-efficient dynamic Monte Carlo simulations of lattice polymers on the parallel processes. We employed the commercialized Flash DSC to measure both reversible and irreversible melting behaviors of lamellar polymer crystals and compared the results with parallel molecular simulations. The reversible melting was monitored by the temperature-modulated DSC method [1]. The irreversible melting was monitored by the power-law heating-rate dependence of superheating [2]. The new insights on the microscopic mechanism of polymer crystal melting and growth at high temperatures were discussed.

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References


Thermodiffusion relates to diffusive mass transport in fluid mixtures that is driven by a temperature gradient. The strength of the effect is measured by the Soret coefficient. Based on a database of ten compounds, for which the Soret coefficients of almost all possible equimolar mixtures had been determined, we have developed a phenomenological description of thermodiffusion that is based on thermophobicities of the pure compounds, which are related to the heats of transport [1]. The same model turned out to hold also for an extended database of 23 substances and 77 out of 253 possible binary mixtures [2]. The substances can be ordered according to their thermophobicity (their tendency to migrate to the cold side), with cis-decalin being the most thermophobic and hexane the most thermophilic one. Based on the determined thermophobicities and the (isothermal) activity coefficients, which are equilibrium properties, the Soret coefficient of any binary mixture of substances that are linked to the existing data base can be calculated. We have also analyzed the composition dependence of the Soret coefficients and the heats of transport for 22 selected binary mixtures. Both the interpretation of the heats of transport in equimolar mixtures as pure component thermophobicities and the composition dependence of the Soret coefficient can be understood on the basis of the thermodiffusion theory developed by Morozov [Phys. Rev. E 79, 031204 (2009)], according to which the composition dependence is caused by the excess volume of mixing.

References

However important the absolute temperature $T$ may be, it is the mean thermal energy $U$ per particle which play a fundamental role in statistics [1]. This leads to determine $D(E,U)$ the density of probability per unit of energy for the energy $E$ of the particles. The problem is to show that the total energy of a given volume of gas shall be calculated by summing, on small segments of energy, the number of atoms with energy on these different segments. For a number $N$ of atoms, this sum should be equal to $N$ times the average $U$ value per atom of thermal energy. To respect the average value of the energy; it should also be that the total probability on the set of the possible energy values must be equal to unity. To solve the problem it should be noted that the energy exchanges that produce high or low energy particles are less probable than those who leave particles in the vicinity of the average value. There is therefore a maximum of statistical weight determining the probability value around average value. On the other hand it is their own volume which forbids two particles to occupy the same place but not the exclusion principle of Pauli. The study of the variations of $UD(E,U)$ as a function of $E/U$ shows that the highest values are in the vicinity of energy zero. This result is normal because if one atom has a very high energy, it should be that a large number of other atoms have ceded a large part of theirs in order to respect the average $U$. Taking the parallel with money this is to say that it takes a lot of poor to make one rich. The complete resolution of the statistical function leads to the following expression:

$$D(E,U) = \frac{\alpha}{[AU][1+\exp(\alpha(E/U-1))] \text{ with } A = 1.7054 \text{ and } \alpha = 1.5049}$$

Let us consider the condensation of a gas. When the temperature $T$ of a gas decreases the density of probability around zero Kelvin tends to infinity. The corresponding probability tends to one. Let then $E_g$ be the heat of vaporization or sublimation. To belong to the gas the atoms must have energy higher than $E_g$. The kinetic energy $E$ of the atoms of the gas is the amount of their energy above $E_g$. When the corresponding mean value $U$ tends to zero, the gas will tends to condense in a liquid or a solid. This result is natural and can be considered as a necessary condition to which $D(E,U)$ must satisfy. The fact that the high $T_c$ superconductors are oxides suggests the formation of obstacles to current flow when the temperature rises. Hypothesis of soft collisions on these obstacles during which the electron gives its energy gives a good account for explanation of the resistivity of these oxides or metals in general. The model also takes into account of the transition to the superconducting state; at low temperature the obstacles related to thermal disorder disappear and the compound becomes superconducting [2,3].

References

The electrocaloric effect (ECE) has been known for many decades, however, the relatively small ECE observed (less than 2.5 K), made it unsuitable for practical applications. Recently, however, materials with large ECE have been predicted and discovered thus opening the possibility of realizing dielectric refrigeration that has several potential advantages in comparison to other cooling technologies [1,2], including better energy efficiency. The recent findings of large ECEs in relaxor ferroelectric polymers have attracted great interest for developing new cooling technology that is more environmentally friendly than the existing cooling technologies [3,4]. A review of recent ECE findings obtained in polymeric ferroelectric and relaxor materials will be given. Besides the materials progress, recent advances in development of practical cooling devices utilizing different approaches and materials will be presented [5].

References

TG and DSC Analysis of Blended Binder Based on Waste Ceramic Powder and Portland Cement

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The cement production has high negative impact on the quality of environment, and its sustainability is open question for material researchers and producers. Worldwide, the cement industry alone is estimated to be responsible for about 7% of all CO2 generated. Additionally, the cement production requires high energy impact, which is approximately 850 kcal per kg of clinker. To ensure the future competitiveness of concrete as a building material, it is essential to improve the sustainability of concrete structures. Therefore, the replacement of cement in concrete by any type of industrial waste represents a tremendous saving of energy and has important environmental benefits. In this paper, possible usage of waste ceramic powder in blended binder is studied. At first, chemical composition of Portland cement and ceramic powder is accessed using XRD. The fineness of ceramics milling is characterized by specific surface and particle size distribution measurement. The pozzolanic activity and the hydration process of the blended binder with ceramics amount varying from 0 to 40 mass% of the cement is researched using the differential scanning calorimetry (DSC) and thermogravimetry (TG). The DSC and TG measurements are done for 2, 7, and 28 days wet cured samples in order to monitor the rate of hydration. The investigation is performed in an argon atmosphere in the temperature range from 25 °C to 1 000 °C with a rate of 5 °C/min. The obtained results show changes in the chemical composition of the studied blended binder at high temperatures, and document the pozzolanic activity of applied ceramics. The temperature and enthalpy of the C-S-H dehydration, portlandite and calcite decomposition are distinguished, and the changes of portlandite amount are accessed in dependence on time of hydration.
Theoretical and Experimental Research on the Flammability of HFO-1234ze(E) and HFO-1234ze(E)/HFC-161

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The use of HCFCs (hydrochlorofluorocarbons) refrigerants and their traditional substitutes (such as R410A, R407C etc.) are not environmentally friendly, since they possess the slight ozone depletion potential (ODP) and large global warming potentials (GWP). As one of the candidates of the new generation refrigerants, HFO-1234ze(E) possesses the suitable thermodynamic properties and small climate change effects. Researchers have studied the possibility of using HFO-1234ze(E) as a refrigerant in chillers. However, its flammability has not been determined completely. This paper contributes to the fundamental flammable characteristics and influence mechanism of HFO-1234ze(E) as well as its blends mixed with refrigerant HFC-161 (fluoroethane) theoretically and experimentally. Firstly, the flames were investigated under various testing conditions. And then the influences of humidity of air and the lubricating oil on the flammability limits of HFO-1234ze(E) were tested and analyzed. The results indicated that the water vapor played an obvious impact on the flammability of HFO-1234ze(E), leading to the flammability ranges of about 7.4% in volumetric concentration. As for the lubricating oil, the influence on flammable characteristic of HFO-1234ze(E) depended on the mixing conditions. Thirdly, both the lower flammability limits (LFLs) and upper flammability limits (UFLs) of HFO-1234ze(E)/HFC-161 were tested under ten different concentration ratios. The results showed that HFO-1234ze(E) possesses a slight flame suppression effect on HFC-161 but could not make it unburnt completely under the experimental conditions.
Diffusion is one of the most ubiquitous transport processes and is often thought to be one of the simplest dissipative mechanisms. Fick's law of diffusion is derived in most elementary textbooks, and relates diffusive fluxes to the gradient of chemical potentials via a diffusion coefficient that is typically thought of as an independent material property. In this talk we will discuss the microscopic and mesoscopic mechanism of diffusion in liquids, for both molecular diffusion and diffusion of colloidal particles. Through a combination of theory and simulations I will demonstrate that diffusion in liquids is, in fact, a rather subtle process due to the crucial contribution of hydrodynamic momentum fluctuations. Using multiscale analysis we derive a closed form stochastic diffusion equation that captures both Fick's law for the ensemble-averaged mean and also the long-range correlated giant fluctuations in individual realizations of the mixing process. These giant fluctuations, observed in experiments, are shown to be the result of the long-ranged hydrodynamic correlations among the diffusing particles. Through numerical experiments we demonstrate that mass transport in liquids can be modeled at all scales, from the microscopic to the macroscopic, not as irreversible Fickian diffusion, but rather, as reversible random advection by thermal velocity fluctuations. Our model gives effective dissipation with a diffusion coefficient that is not a material constant as its value depends on the scale of observation. We also use computer simulations to study the static and dynamic spectrum of concentration fluctuations in confined systems and compare to experimental results and simple (linearized fluctuating hydrodynamics) theories. We study both transient dynamics in the GRADFLEX experiment, performed in microgravity, as well as experiments performed on Earth, where gravity plays a key role.
pH-Driven Reversible Aqueous Biphasic Systems Composed of Ionic Liquids

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Recently, a large interest has been devoted to the exploitation of dynamic and reversible biphasic systems constituted by ionic liquids (ILs) [1]. It was previously demonstrated that mixtures involving ILs and other solvents can be switched between the homogeneous regime and a two-phase system either by a temperature-driven phenomenon or by adding CO$_2$/N$_2$ [1]. These systems have shown to be remarkable in the selective separation of several value-added compounds, such as proteins [1]. Amongst the liquid-liquid extraction techniques, aqueous biphasic systems (ABS) constitute a “greener” and more benign and biocompatible option since they are mainly composed of water (ca. 50 wt%). Furthermore, these systems can lead to the complete extraction of a wide variety of compounds and to high concentration factors [2]. In addition to all the advantages and enhanced performance of IL-based ABS, their switchable character between a two-phase and a homogeneous regime was not previously attempted. The major goal of this work consists on the exploitation of switchable IL-based ABS triggered by a pH-dependent phenomenon. A large array of ABS, obtained by the combination of potassium citrate with different ILs, was initially investigated by the determination of their ternary phase diagrams at different pH values. The first set of reversible IL-based ABS was ascertained by the addition of citric acid or potassium hydroxide and through the organic salt speciation. Their reversibility behaviour was demonstrated for at least 3 times. In addition to IL-salt mixtures, polymer-IL-based ABS were also investigated while reaching their switchable behaviour through the IL anion speciation. Finally, these ABS were explored as fractionation techniques for amino acids and peptides.

Acknowledgements

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References

With the increasing maturity of conventional oil resources and limited volumes of new conventional resources to replace production, attention has been focused on viscosity reduction to enhance oil production from brown-field reservoirs by the injection of light gases such as CO2. Also, viscosity plays a significant role in managing and controlling injection of CO2 into depleted oil reservoirs or saline aquifers for the purpose of carbon sequestration.

In this study, an experimental measurement on viscosity and density of mixtures of crude oils and CO2 was performed using accurate technique such as vibrating-wire viscometer. However, for viscosity measurements involving crude oil using vibrating-wire viscometer, asphaltene precipitation and deposition can be a problem. This problem can have effects on the viscometer sensor, flow lines and fittings and introduced a significant error that can affect the accuracy of the results. Therefore, the ASTM recommended procedure (ASTM2007-80) for separating asphaltene was modified to obtain representative crude oils free of asphaltene. The range of temperature was (273.18 to 453) K while that of pressure was (0.1 to 130) MPa. The experimental data will be used for modelling of the viscosity of crude oil + CO2 at elevated pressure and temperature using appropriate model for improved prediction of the CO2-crude oil mixture under persistently changing conditions of composition, pressure, temperature and conditions common with reservoir fluids.
We measured the degree of polarization $P$ of the light emitted in the wavelength range 1 to 12 micron from thin tungsten and cobalt wires heated from a little above room temperature up to melting. The wire diameters are 9, 25, and 50 micron. For all samples the emitted light is partially polarized perpendicularly to the wire axis. $P$ varies from roughly 30% at relatively low temperature ($T \sim 500$ K) for both materials down to 17% for tungsten at melting ($T \sim 3700$ K) and to 7% for cobalt at melting ($T \sim 1770$ K). For tungsten the variation of $P$ with $T$ is smooth. Its behavior can quite satisfactorily be reproduced by the theory of scattering of electromagnetic waves off a cylindrical metal object in spite of the great uncertainties of literature data on tungsten emissivity and provided that an accurate extrapolation is carried out of the Drude parameters for the tungsten dielectric constant, which are given in literature only for a limited wavelength (<2.65 micron) and temperature (<2400 K) range. For cobalt the transition from high- to low polarization degree is sharper than in tungsten. It apparently takes place in a temperature range between the structural hip->fcc martensitic transition (~670 K) and the ferro-paramagnetic Curie transition (~1400 K.) The observed variation of $P$ with $T$ also shows a hysteretic behavior. As no data on the temperature and wavelength dependence of the dielectric constant of cobalt are available in literature for the wide ranges we explored, we have not been able to compute the prediction of the electromagnetic scattering theory. Thus, the cobalt data are the first measurements of this kind and still deserve to be fully rationalized.
Determination of Phase Equilibria for the Mixture (CO$_2$+ CH$_4$)

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High-pressure phase equilibrium data are often complex and difficult to predict and it is necessary to obtain some experimental data. The electric permittivity or dielectric constant is a physical property that can be defined as the electric polarization acquired by the molecules of a substance as a result of the induction generated by an electromagnetic field. It is an extensive property which depends on temperature and pressure $\varepsilon(p,T)$. Based on this property has been developed a measurement technique which consists of a cylindrical resonant cavity that works in the microwave band; a sapphire tube with the sample is located inside this cavity. The resonant modes of cylindrical cavity depend on the electrical properties of the sample. For example, a liquid sample is maintained at constant temperature and the pressure is decreasing until the first bubble occurs, this phase transition presents a discontinuity in the electric permittivity and therefore in the resonant modes of the cavity. With the reverse procedure it is possible to measure the dew point. With this technique, the equilibrium data of fluid mixtures at high pressure are measured applying the synthetic method. This technique can be an alternative to the traditional visual synthetic method. The technique was checked and it has been used for measuring the phase behaviour of the binary mixture (CO$_2$ + CH$_4$) which results are presented.

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The Role of Curvature in Vapor-Liquid Nucleation

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Nucleation is of fundamental interest in science and technology, and has been widely investigated by experiments, theory, and simulations. Classical nucleation theory is still the most widely used theoretical tool to predict nucleation rates, however, its predictions are often orders of magnitude away from simulations and experiments. One of the crudest assumptions of classical nucleation theory is the neglect of curvature dependence in the surface tension and the nonequilibrium transfer properties. In our work, we discuss the role of curvature in vapor-liquid nucleation. We show that the surface tension of a small bubble/droplet deviates significantly from that of the planar interface, and that the heat and mass transfer coefficients of the bubble/droplet are highly curvature dependent. By expanding the properties in the curvature, we derive a consistent description of the steady-state non-isothermal nucleation rate using nonequilibrium thermodynamics. The coefficients in the curvature expansions are obtained by combining density functional theory with nonequilibrium molecular dynamics. Results will be presented first for the Lennard-Jones fluid as a benchmark example, and then for water. By comparing the results to classical nucleation theory and experiments, new and important insight will be given on how curvature affects nucleation rates.

References

Guards Hot Plate (GHP) is recognized as a precise method for thermal conductivity/resistance measurement mainly focused on thermal insulating materials. For measurements at moderate temperatures, GHP is well established e.g. in building industry enabling the determination of thermal conductivity with an uncertainty lower than 2%. GHP is a steady-state method based on Fourier’s law of heat conduction. The specimen is sandwiched between two plates with different temperature which leads to setting a temperature gradient through the specimen. From the knowledge of the geometrical properties (contact surface area and specimen thickness) and hot plate heating power at steady state conductivity can be evaluated. High-temperature region brings many limitations and challenges to GHP method: Narrower range of materials can be used, disrupting of desired temperature profile in the specimen due to heat losses has to be minimized and high accuracy of temperature measurement has to be maintained. As a consequence, the uncertainty of the thermal conductivity measurements using GHP is rather high. Recently, Czech Metrology Institute (CMI) developed High-Temperature Guarded Hot Plate (HTGHP) apparatus allowing maximum operating temperature 850 °C and target uncertainty of measurement lower than 5%. With this apparatus CMI is involved in European Metrology Research Programme (EMRP) project SIB52 Thermo in which one of the tasks is to improve European equivalence in thermal conductivity measurement up to 800 °C. The apparatus design, results of preliminary measurements together with the current uncertainty budget will be presented.
Based on two previously obtained generalized equations of state, which describe the properties of hydrocarbon chain and cyclic structures, a method for the predictive calculation of thermodynamic properties and phase equilibria of complex hydrocarbon mixtures (oil and gas condensate fractions) has been developed. The method is applicable over a temperature range from freezing to 700 K at pressures up to 100 MPa, including the liquid and gas phases, and the supercritical region. The calculation of thermodynamic properties is made within the framework of the extended three-parameter corresponding states principle. The acentric factor was chosen as the determining criterion of similarity. The complex hydrocarbon mixture is treated as an individual substance, known from physical chemistry as a single-fluid model. In this model, the mixture is a hypothetical individual hydrocarbon with an effective molar mass $M$ and pseudocritical properties $T_{pc}$, $\rho_{pc}$, and $\rho_{pc}$. This hydrocarbon is characterized by the content of paraffin and cyclic structures in an effective molecule. The paper outlines the method and the results of testing on more than 300 oil and gas condensate fractions. In addition, the results obtained from cubic equations and a generalized equation of Kessler and Lee is presented. For the calculation of phase equilibria, a method for modeling the composition of complex hydrocarbon mixtures using pseudocomponents (subfractions) has been developed based on the distillation curve and a minimum set of physical and chemical properties of mixtures consisting of average boiling temperature, relative density, and molar mass. Rules for the transition from the single-fluid model of the substance used to calculate thermodynamic properties to the linear model of the mixture, from which phase equilibria can be calculated, have been developed. The phase equilibria results (dew points and bubble points) for the hydrocarbon mixtures from the proposed methods and cubic equations are presented. The accuracy of the predictive calculation of phase equilibria is approximately the same for both the multiparameter and the cubic equations of state. However, the accuracy of other thermodynamic properties, such as density, from the multiparameter equation is substantially better.
A New Class of Equations of State in the Density Scaling Regime

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In the last decade, one of prominent trends [1] in investigating the glass transition and related phenomena has relied on the density scaling law obeyed by molecular dynamics of various materials from different material groups such as supercooled van der Waals liquids, supercooled ionic liquids, polymer melts, and liquid crystals. According to the scaling law, dynamic quantities such as structural relaxation times (or segmental relaxation times in case of polymers), viscosities, and diffusivities can be scaled onto one master curve that is a function of the single scaling variable \((\text{density}^\gamma)/\text{temperature}\) with the scaling exponent \(\gamma\) suggested to be straightforwardly related to the exponent \(3^*\gamma\) of the repulsive inverse power law that dominates the effective short range intermolecular potential valid for viscous liquids. Based on the relevant potential, we have derived [2-4] new equations of state (EOSs) in the density scaling regime and very successfully applied them to describe volumetric data of various materials (van der Waals liquids, ionic liquids, polymer melts, and associated liquids) measured in the pressure range \(0.1\text{MPa} \leq p \leq 200\text{MPa}\). We have confirmed theoretical grounds for the EOSs by molecular dynamics simulation studies [3,5] and well defined applicability ranges of them and physical meanings of all their parameters. We have shown that the EOSs can be also used beyond the supercooled region. Very recently, we have successfully applied [4] them to investigate a complex, volumetric response of simple liquids measured by the scanning transiometry.

References

Simultaneous Determination of Thermal and Mutual Diffusivity of Binary Mixtures of n-Alkanes with Carbon Monoxide, Hydrogen, and Water by Dynamic Light Scattering

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In the present study, it is demonstrated that thermal and mutual diffusivities of binary mixtures of the n-alkanes n-dodecane (n-C_{12}H_{26}), n-octacosane (n-C_{28}H_{56}), and n-tetracontane (n-C_{40}H_{82}) with carbon monoxide (CO), hydrogen (H\textsubscript{2}), and water (H\textsubscript{2}O) are simultaneously accessible by dynamic light scattering (DLS). As the light scattering signals originating from thermal and concentration fluctuations appear in similar time scales, different data evaluation strategies were tested to achieve minimum uncertainties in the resulting transport properties. To test the agreement of the respective theoretical model with the DLS signals in the regression, an improved multi-fit procedure is introduced. With the selected data evaluation strategy, expanded uncertainties (k = 2) of 4 to 15% and 4 to 30% in the thermal and mutual diffusivities could be obtained for the binary mixtures. The mutual diffusivities for the mixtures measured at temperatures ranging from 398 to 523 K and pressures of 5 to 30 bar at saturation conditions are in agreement with molecular dynamics (MD) simulations using atomistic models and with experimental data from literature.
Investigation of Ternary Mixtures of $n$-Alkanes and Gases by Dynamic Light Scattering

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It is still an open question which information can be expected from dynamic light scattering (DLS) experiments for ternary mixtures. A theoretical approach suggests that DLS signals originating from ternary mixtures could be governed by fluctuations in temperature and two individual contributions connected with fluctuations in concentration which are related to the Fickian diffusion matrix. Until now, this approach could not be proven appropriately by experiments. In the present study, ternary mixtures consisting of $n$-dodecane ($n$-C$_{12}$H$_{26}$) and $n$-octacosane ($n$-C$_{28}$H$_{58}$) with dissolved hydrogen ($H_2$), carbon monoxide (CO), or water ($H_2O$) are considered as model systems. To provide a reliable data base for comparison, the thermal diffusivity of the pure substances and also the mutual diffusivities of their binary mixtures which constitute the ternary mixtures were investigated. For the ternary mixtures, three different signals could be distinguished from the time-resolved analysis of the scattered light intensity by using photon correlation spectroscopy. It could be evidenced that the signals are clearly associated with hydrodynamic modes as suggested by the theoretical approach. The fastest mode observable for a ternary mixture matches with the mode associated with the thermal diffusivity in the corresponding binary $n$-alkane mixture. The two further modes obviously connected with the molecular mass transport are observable on different time scales. These two modes in the ternary mixture are comparable to the modes associated with the concentration fluctuations in the corresponding binary mixtures.
Coarse-Grained Models for Particle-Stabilized Fluid-Fluid Interfaces using GENERIC and Simulations

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In emulsions, foams, and dispersions of soft core-shell particles, interfacial properties such as the surface shear modulus, the dilatational modulus, the bending rigidity, and transport coefficients for mass and energy across the interface, have a significant impact on their stability, and their response to applied deformations and temperature gradients (L.M.C. Sagis, Rev. Mod. Phys, 83 (2011) 1367). This is particularly true for systems with interfaces stabilized by anisotropic particles (Pickering stabilization). These particles tend to self-assemble at the interface into complex (quasi-) two-dimensional microstructures. Depending on surface area fraction and the interactions between them they can form 2D isotropic dispersions, 2D gels, 2D glasses, or 2D liquid crystalline phases. Applied deformations and temperature gradients can cause changes in these microstructures, which often lead to a highly nonlinear response of the system to perturbations. Constitutive models capable of describing this behavior at realistic surface area fractions of particles are still scarce. In this presentation we will discuss how the GENERIC framework in combination with particle-based simulation methods (MC and EDMD) can be used to obtain constitutive models for the behavior of interfaces stabilized by hard ellipsoids. We will focus in particular on the mechanical properties of such an interface in steady and oscillatory deformations, at area fractions ranging from the dilute isotropic regime, to the nematic phase. The model is capable of predicting the experimentally observed shear thinning behavior of this type of interfaces in steady surface shear, and the anisotropies which are observed in the Lissajous plots of surface stress versus strain, in oscillatory dilatational experiments.
Characterization of Vertical Cracks Using Burst Vibrothermography

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The detection and characterization of kissing vertical cracks is a challenging task. Standard non-destructive evaluation techniques currently applied to detect surface breaking and shallow subsurface cracks, like liquids penetrants and Eddy currents, are not able to size the in-depth extent of the crack accurately. Ultrasound excited thermography (vibrothermography) has demonstrated its capability to detect defects such as cracks or delaminations in a wide variety of materials both in modulated and burst regimes. In vibrothermography the sample is excited with ultrasounds and at the defects heat is produced because of friction between the defect faces. The surface temperature rise above the defect can be measured by an infrared camera. In a previous work, we developed a stabilized inversion algorithm to characterize vertical cracks from lock-in vibrothermography data obtained at several modulation frequencies. The drawback of this approach is that data taking is rather time consuming. In this work, we present a method to characterize vertical cracks from burst vibrothermography data, in which data taking is much faster. We compute the evolution of the surface temperature distribution when a sample containing a vertical crack is excited by means an ultrasound burst. By inverting synthetic data with added white noise we have analyzed the accuracy of the method to characterize the size and position of the crack depending on the burst duration and the noise in the data. Finally, we have prepared samples containing calibrated inner heat sources of different shapes. The inversions of experimental data obtained from the calibrated samples confirm the capability of the method to characterize vertical cracks.
High-temperature properties of carbon and refractory carbides are of interest for the aero-space industry and nuclear technologies (a matrix of nuclear fuels). It is known that zirconium carbide is used as a protective high-temperature covering, i.e. in the form of rather thin layers. In present work the microsecond technique of electrical pulse heating which gives uniform energy input into a film specimen is considered. ZrC+C specimens in the form of a thin layer (4.9 microns) sputtered on isolating substrates by magnetron sputtering technique were used. Specimens contained (at. %): Zr – 17.88; C – 67.69; N – 8.13; O – 5.98. Imparted energy, resistivity (referred to the initial size of a specimen), normal spectral emissivity and specific heat were measured in the temperature range of 2100 – 4500 K. The heating rate was on the order of $10^9$ K/s. To obtain true temperature of the specimen the wedge-shaped blackbody design was used. The obtained results are compared with the equilibrium Zr-C phase diagram. The solid-liquid phase transition (melting) begins at 3150 K and finishes at 3640 K. Thus the obtained temperature for the start of melting almost coincides (taking into account an uncertainty) with the temperature of the eutectic isotherm for the equilibrium phase diagram. The phase diagram shows that the composition with atomic ratio C/Zr = 3.8 (our case) corresponds to the liquidus ~ 4000 K, and we obtained 3640 K. Possibly this discrepancy may be caused by large amounts of impurities.
Density Measurements under Pressure for the Binary System Di-Isopropyl Ether + 1-Hexanol at Temperatures up to 353.15 K and at Pressures up to 100 MPa

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Tertiary alkyl ethers like di-isopropylether DIPE, having similar properties (e.g., vapour pressures) to hydrocarbons and the potential to increase the octane number and to decrease the emission of carbon monoxide, have become important additives for gasoline. The ethers increase the amount of oxygen in gasoline in order to reduce the CO content in the exhaust gas of automobiles. DIPE, pure or mixed with alkanols or alkanes, has been recommended as a high octane blending agent for motor gasoline. Ether + alcohol mixtures are of interest as model mixtures for gasoline in which the ether and the alcohol act as non-polluting, high octane number blending agents. Despite of this interest, density data of binary mixtures containing ether + alcohol at pressures other than the atmospheric pressure are very scarce in the literature. Density of the binary mixture DIPE + 1-hexanol have been measured under pressure and reported in this work using a vibrating tube densitometer. No literature date on the density at high temperature and pressure for the same binary mixture has been found. Experimental densities for the binary system DIPE + 1-hexanol have been measured at 298.15, 313.15, 333.15 and 353.15 K and at nineteen isobars up to 100 MPa. For each composition, the experimental values were correlated using a Tait-type equation. Furthermore, the excess molar volume and the isothermal compressibility were calculated from the density data. This paper is part of the Doctoral Thesis of A. Shriyer.
Quartz crystal microbalance (QCM) is capable of simultaneous measurement of diffusivity $D$ and solubility $S$ of gases in thin film samples due to exceptionally high sensitivity to the sample's areal mass density $m$ ($\approx 1 \text{ ng/cm}^2$). Since one side of the sample has to adhere to a QCM sensor (typically a 1 inch diameter, 0.33 mm thick quartz disk with thin metal electrodes), $D$ can be measured only in a transient diffusion experiment, by recording a thin film sample's $m$ as a function of time after a step-change in penetrant gas's pressure and then fitting a theoretical equation to the experimental data by adjusting both $D$ and $S$. This presentation shows how for all three studied gases (nitrogen, carbon dioxide, and iso-butane) the transient diffusion across a spin-cast glassy polymer film exhibits non-Fickian behavior, which is best modeled by Dual Diffusion Model (DDM) introduced by L.Wang et al. in 2012. The DDM postulates independent diffusion of penetrant’s molecules occupying two types of absorption sites in the polymer matrix with corresponding values of diffusivity and solubility for each of the two concurrent mechanisms.
another test

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It is well known that thermodynamics allows calculation of calorimetric properties for fluids from equations of state using experimental pressure/density/temperature data. However, the technique has found little use because these data lacked enough accuracy to approach calorimetric measurements. However, with the introduction of highly accurate magnetic suspension densimeters, it has become interesting to check the technique once again.

The approach of this work is to use an analysis of experimental first and second derivatives of pressure with respect to temperature at constant density along with residual properties to determine energies, entropies and heat capacities. Those derivatives can come from fitting isochoric data or from using numerical differentiation. The uncertainty of the heat capacities is a function of the uncertainty of the fit used to characterize the isochoric data and the impact of using numerical and analytical derivatives to solve for real properties. This work applies the methodology to experimental isochoric and isothermal data of a ternary mixture with mole fractions of 0.95014 methane, 0.03969 ethane and 0.01017 propane. The matrix of the data contains 10 isochores and 5 isotherms covering a range of temperature from 140 to 500 K at pressures up to 200 MPa. In addition, the paper proposes a new strategic way to develop experimental design and data acquisition techniques to allow building a complete thermodynamic characterization of fluids using a highly accurate magnetic suspension densimeter (MSD).
Simultaneous Differential Scanning Calorimetry and Thermogravimetric Analysis of Portland Cement As a Function of Age

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We study the hydration and pozzolanic reactions of ordinary Portland cement as a function of age, using the differential scanning calorimetry and thermogravimetry. The measurements are done for 1, 2, 7, 28, 90, and 180 days cured samples in order to monitor the rate of hydration. The investigation is performed in the temperature range from 25 °C to 1000 °C with a heating rate 5 °C/min in an argon atmosphere. The temperature, enthalpy, and mass change during the decomposition of calcium silicate hydrate gels, portlandite, and calcite are determined, and the changes in the portlandite amount are estimated in dependence on the time of hydration. In addition, the peaks due to the formation of ettringite are found.
Equations of Liquid-Vapor Equilibrium in Binary Mixtures of Krypton with Air Components

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For binary mixtures dependence of coexisting phases, pressure from temperature and composition is determined by the correlation between temperature of mixture and critical temperatures of components. To calculate the liquid and vapor pressures at phase equilibrium at temperatures below the critical temperatures of components we used the equation:

\[ p' = p_s + (p_{s1} - p_{s2}) \sum M'_k x^j (1-x)^{j-k} T^{j-k}, \]

where \( p' \) is liquid pressure, \( p_s \) is linear combination of the saturation pressures of components, \( p_{s1} \) and \( p_{s2} \) are saturation pressures of components with low and high boiling points, \( x \) is molar concentration of a low–boiling point component in liquid phase, \( T \) is absolute temperature, \( M'_k \) are coefficients of equations. Equation for vapor pressure \( p'' \) has an identical form with coefficients \( M''_k \) and concentration \( y \). Equation satisfies limiting conditions: \( p_{\text{mix}} \to p_{s1} \) at \( x \to 0 \) and \( y \to 0 \) and \( p_{\text{mix}} \to p_{s2} \) at \( x \to 1 \) and \( y \to 1 \). The effectiveness of equation was verified using experimental data for mixtures krypton-nitrogen (40 points, \( T = 100-125 \) K, \( p = 0.13-1.45 \) MPa), krypton-oxygen (122 points, \( T = 84-148 \) K, \( p = 0.068-0.69 \) MPa) and krypton-argon (199 points, \( T = 90-149 \) K, \( p = 0.023-4.4 \) MPa). Pressures of components and values \( p_s \) were calculated from exact equations for vaporization curves. Coefficients \( M_k \) were determined by least squares method, number of coefficients was 2-4. Root-mean-square deviations \( \delta p' \) and \( \delta p'' \) of experimental data from calculated are 2.98-4.09 %. The obtained equations allow to define third parameter of phase equilibrium if other two are known. Calculated values of \( x, y, T' \) and \( T'' \) showed good agreement with experimental data. Root-mean-square deviations \( \Delta x, \Delta y, \Delta T' \) and \( \Delta T'' \) of experimental data from calculated are respectively 0.010-0.024, 0.013-0.024, 0.412-0.503 K, 0.484-0.607 K. Thus, used equation is suitable for describing phase equilibrium in binary mixtures at temperatures below the critical temperatures of components.
Simultaneous Measurements of Electrical and Thermal Conductivity as well as SAXS/WAXS during Crystallization of Polycaprolactone/MWCNT Composites

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In situ crystallization of poly(ε-caprolactone) (PCL) filled with different contents (0.2 - 5 wt.%) of multiwalled carbon nanotubes (MWCNTs) was investigated in X-ray (SAXS/WAXS) synchrotron experiments simultaneously with thermal and electric conductivity measurements. The combined study provides information on nucleation ability of MWCNT, crystallization and melting kinetics, degree of crystallinity as well as the evolution of thermal diffusivity and electrical conductivity of PCL/MWCNT composites during isothermal and non-isothermal crystallization. MWCNTs act as strong nucleation agents. Two separate melting peaks in calorimetric experiments indicate (i) nucleation by the nanotubes and (ii) heterogeneous nucleation by the polymer itself. Electrical conductivity measurements showed for MWCNT contents above 0.5 wt% an increase in electrical conductivity by more than one order of magnitude, which can be related to the formation of a conductive nanotube network. At the same time, thermal conductivity of the composite is increasing only slightly, which is rather related to the increase of the crystalline phase than to heat transfer in a percolated structure. The dependence of thermal conductivity on MWCNT content can be related to the addition of filler with high thermal conductance and does not show a simple correlation to the electrical conductivity.
Following carbon dioxide injection in deep saline aquifers, CO₂ dissolves in the formation brines forming acidic solutions that can subsequently react with host reservoir minerals, altering both porosity and permeability. The direction and rates of these reactions are influenced by several factors including properties that are associated with the brine system. Consequently, understanding and quantifying the impacts of the chemical and physical properties of the reacting fluids and their effect on overall reaction kinetics is fundamental to predicting the properties of the injected CO₂. In this work, we present a thorough experimental study of the properties of different brine systems by varying ionic strengths and ionic species. The impact of these variables on rock-fluid chemical reactions is examined. Using a rotating disk technique, we have investigated the chemical interactions between CO₂-saturated brines and carbonate minerals such as calcite and dolomite at pressures (up to 15MPa) and temperatures (up to 353K)- conditions pertinent to carbon storage. Kinetic parameters derived from the study are subsequently applied to our previously derived computer model.
New Class of Self-Buffering Ionic Liquid and Its Application for Separation of 1,3-Dioxolane from its Azeotropic Aqueous Solution

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In this work we synthesized a new self-buffering and biocompatible ionic liquid, in which anion was derived from a commonly used biological Good buffer (GB), 4-(2-hydroxyethyl)-1-piperazinepropanesulfonic acid (EPPS) and cation was contributed from tetramethylammonium (TMA). The buffering action of this new synthesized Good buffer ionic liquid (GBIL) is confirmed by measuring its pH profile in aqueous solution. Moreover, the pKa values of the GBIL in water were determined experimentally at 293.2 K, 298.15 K and 308.15 K. It was also found that the presence of this new GBIL, [TMA][EPPS], in 1,3-dioxolane aqueous solution could induce liquid-liquid phase splitting. The influence of this new GBIL on the separation of 1,3-dioxolane from its aqueous solution has been investigated by measuring solid-liquid-liquid equilibrium (SLLE) and liquid-liquid equilibrium (LLE) data for the 1,3-dioxolane + water + GBIL system under atmospheric pressure and at 298.2 K. The experimental LLE tie-line data were correlated well with the NRTL model and their consistency has been confirmed by correlating the LLE tie-line data with the Othmer-Tobias equation. The experimental results also indicated that this new GBIL can be used as an attractive auxiliary agent to recover high purity 1,3-dioxolane from its azeotropic solution. A greener separation process is proposed in the present study. In comparison with the conventional inorganic salts, this new GBIL is a biocompatible, non-corrosive, and green compound.
We report the viscosity and density of sodium chloride, calcium chloride and magnesium chloride aqueous solutions with and without dissolved CO$_2$. The measurements were made in the single-phase compressed liquid region at temperatures between (274 and 449) K at pressures up to 100 MPa. The viscosity was measured with a vibrating-wire viscometer while the density was measured by means of a vibrating U-tube densimeter. The initial results with the vibrating-wire viscometer for NaCl solutions without dissolved CO$_2$ were found to exhibit a systematic error that increased with the electrical conductivity of the brine and hence was worst at high temperatures and high salt concentrations. This issue has been addressed with a semi-empirical modification of the working equation for the vibrating-wire viscometer. Measurements of the viscosity and density in the brines under CO$_2$ addition were made at salt molalities of up to 5 mol·kg$^{-1}$ and are associated with relative uncertainties of 0.1 % for density and 2 % for viscosity. The results for both properties have been correlated as functions of temperature, pressure, salt molality and the mole fraction of dissolved CO$_2$. For viscosity, we used a simple modification of the Vogel-Fulcher-Tamman equation while, for the densities, a modified Tammann-Tait equation, incorporating a correlation of the partial molar volume of dissolved CO$_2$, was employed.
We investigate the behaviour of fluids confined between two walls and under the influence of either a temperature gradient, an external gravitational field, or both effects concurrently. This set up allows us to consider the impact of liquid-solid interfaces on the molecular orientation and density profile of the fluid. The gravitational field and/or temperature gradient act in concert with the induced density gradient to generate a preferred orientation in molecular fluids consisting of anisotropic molecules. We illustrate this general phenomenon in a number of anisotropic fluids and extend the non-equilibrium thermodynamics theory to encompass these new effects. Comparison of this gravity induced orientational effect with the recently discovered thermo-molecular orientation (TMO) effect has led to new insights into both phenomena.

References

Structural and Dynamic Correlations of Alkali Halide Salts in Water/Alcohol Mixtures: a Combined Optical Kerr Effect (OKE) Spectroscopy and Molecular Dynamics Investigation

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Experiments to measure the electromagnetic response of liquids in the terahertz (THz) frequency range, either by dielectric spectroscopy or related non-linear methods like the optical Kerr effect (OKE) can provide valuable insight into the dynamics of intermolecular interactions in aqueous solutions and in particular hydrogen bonding. While aqueous electrolyte solutions have been much studied with these and other methods, salts in mixtures of polar solvents are much less well understood. Water/alcohol mixtures feature non-ideal behavior characterized by strong anomalies in the thermodynamic properties and by the formation of nano-scale water clusters. The changes undergone in the hydrogen bond structure of water and the modification of the dielectric constant provide an interesting medium for ion cluster formation. Improving understanding of these ternary mixtures is especially relevant to electrospray ionization (ESI), where water/methanol mixtures are commonly used as solvents. In this contribution we will discuss the THz response of a system of alkali halide salts in water/alcohol mixtures. This technique in conjunction with molecular dynamics simulations enables a detailed analysis of correlations in mixtures and through the theoretical modelling of the experimental measurements. Our study represents a stepping stone towards using THz spectroscopy to measure the thermo-molecular orientation (TMO) effect, which heretofore has only been observed in computer simulations.
Precise Method for Determining the Enthalpy of Vaporization of Concentrated Salt Solutions using a Bubble Column Evaporator

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The effect of many salts on the inhibition of bubble coalescence allows the construction of a bubble column evaporator (BCE) for the efficient transfer of both vapor and heat. A BCE system was built in this study to determine accurate and precise enthalpy of vaporization ($\Delta H_{\text{vap}}$) values for concentrated salt solutions. This method is based on the steady state volumetric energy balance developed in a bubble column evaporator. The warm dry air continuously flows as fine bubbles through the column and steady state is obtained when the heat supplied to the column equals the heat of vaporization required to reach the equilibrium water vapor pressure within the bubbles. The BCE system offers a novel and simple approach for $\Delta H_{\text{vap}}$ measurements because it only requires measurement of the hydrostatic differential pressure across the column and the temperatures of the steady state column and the inlet gas. In this work, an automatic acquisition system for temperature data was developed in order to study the frequency distribution of $\Delta H_{\text{vap}}$ values, and vacuum insulation of the bubble column was built to reduce heat transfer to the environment. The results obtained for a range of common salt solutions were in good agreement with literature values, within 1% accuracy as well as 1% precision with each measurement. New $\Delta H_{\text{vap}}$ values of Li2SO4 and ZnSO4 solutions were determined and indicate the conditions required to enhance evaporative cooling systems and improve thermal desalination. An analysis was also carried out on the effect of salt concentration on $\Delta H_{\text{vap}}$ and on calculated values of the partial molar enthalpy of dilution ($\Delta H_{\text{dil}}$).
Dielectric-constant gas thermometry (DCGT) performed by PTB is now a well-established method of primary thermometry and a tool for investigating the thermophysical properties (particle interaction, polarizability) of gases. The basic idea of DCGT is to replace the density in the equation of state by the dielectric constant and to measure this constant by the capacitance changes of a capacitor filled with gas at different pressures and constant temperature (measurement of isotherms). Until now the main application of DCGT was the determination of thermodynamic temperature below the triple point of water (TPW, 273.16 K) [1] or, in recent times, the determination of the Boltzmann constant at the TPW for the new definition of the base unit kelvin of the International System of Units [2]. The extreme demands concerning the uncertainty of pressure, capacitance and temperature measurements led to unique experimental capabilities at PTB. This was recently demonstrated by the determination of the virial coefficients of helium [3]. New measurements with argon, neon and helium have been performed. As experimental basis, the thermophysical properties of the capacitor materials (thermal expansion, heat capacity and elastic constants) have been investigated in dependence on temperature, which now allows covering the complete temperature range from 2 K to 300 K. A comparison with literature data verifies the potential of DCGT in gas metrology.

References

The Laboratory for Thermophysical Properties (LTP) is a global service provider for the experimental determination of phase equilibria (e.g., vapor pressures, critical data, VLE, VLLE, or SLE), volumetric data like densities or density changes, caloric data such as enthalpy changes and heat capacities, and transport properties like viscosities, thermal conductivity or surface tension. Carbon capture and acid gas treatment mainly with amine solutions is still a focus in technical developments which resulted in intensive experimental determinations of various properties. Due to the large amount of flue and acid gas and the increasing environmental restrictions, any improvement with new or modified solvents is of high interest. Experimental projects in this field for many international chemical, petrochemical or engineering companies with various solvent-gas combinations were performed at LTP during the last 10 years. Usually all experimental determinations and results are exclusive and secret. Two years ago LTP launched an internal research project with determinations for aqueous MDEA solutions as solvent. For solutions with different carbon dioxide or hydrogen sulfide loadings experimental phase equilibrium data, densities, viscosities, thermal conductivities, surface tensions, heat capacities, and heats of absorption were determined. The results of these determinations will be presented together with the used experimental set-ups. Different methods will be presented like synthetic equilibrium cell, Stabinger viscometer, magnetic suspension balance, transient hot wire and hot plate, pendant drop method, flow calorimeter, or Tian-Calvet calorimeter.
Cloud-point Measurement of Binary and Ternary Systems for the [P(MMA-co-PnFPA)] in Supercritical Fluoric Solvents

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The poly(methyl methacrylate-co-2,2,3,3,3-pentafluorophenyl acrylate) [P(MMA-co-PnFPA)] as a fluoric copolymer was prepared by dispersion polymerization under supercritical carbon dioxide. The copolymers characterization for the P(MMA-co-PnFPA) were investigated with varied mole ratios of MMA vs PnFPA (20:1, 25:1 and 30:1), AIBN amounts (1.0 wt%, 2.0 wt% and 4.0 wt%) and the weight average molecular weight (Mw). Experimental cloud-point up to 453 K and 220 MPa are measured for binary and ternary mixtures of P(MMA-co-PnFPA) in supercritical fluoric solvents (CH2F2, CHF3 and CHClF2). Phase behavior of binary system for the P(MMA-co-PnFPA) [25:1, AIBN: 1.0 wt% (Mw=173,000), 2.0 wt% (Mw=93,600), and 4.0 wt% (Mw=74,600)] + CH2F2 (or CHF3 and CHClF2) mixtures at temperature range from 333 K to 434 K and pressure up to 153 MPa are measured the upper critical solution temperature (UCST) type behavior with negative slope for the P(MMA-co-PnFPA) + CH2F2, and lower critical solution temperature (LCST) type curve with positive slope for the P(MMA-co-PnFPA) + CHF3 and P(MMA-co-PnFPA) + CHClF2 mixtures. Cloud-point curves for the P(MMA-co-PnFPA) [20:1 (Mw=170,000), 25:1 (Mw=173,000), and 30:1 (Mw=228,000); 1.0 wt% AIBN] + supercritical (CH2F2, CHF3 and CHClF2) mixtures show a negative slope for the P(MMA-co-PnFPA) + CH2F2, and a positive slope for the P(MMA-co-PnFPA) + CHF3 and P(MMA-co-PnFPA) + CHClF2 mixtures at temperature to 453 K and pressure up to 160 MPa. Also, the impact of MMA on phase behavior for the P(MMA-co-PnFPA) [25:1; 1.0 wt% AIBN] + CH2F2 mixtures are measured in changes of the pressure-temperature (p, T) slope from UCST behavior to LCST behavior, and with MMA cosolvent concentrations of (0.0 ~ 28.9) wt%.
An apparatus to measure the viscosity of gases using a wire clamped at both ends has been constructed. The analysis includes methods that reduce the uncertainty of the reported viscosity. The performance of the apparatus and model have been verified by measuring the viscosity of pure gases methane, carbon dioxide, and nitrogen, and relative deviations from literature are all less than 1%. Further, more stringent tests of the apparatus using the viscosity ratio of two gases show less than 0.4% difference from literature. A commercial vibrating tube densimeter has been installed to enable the measurement of the density of the same mixture simultaneously with the viscosity measurement, which eliminates the reliance on an equation of state to calculate viscosity. The viscosity was obtained from both the steady state and ring-down (transient response) techniques and compared, and an analysis performed on the optimal regimes for each measurement method. In addition, a novel measurement technique is presented which allows accurate measurements of the transient response without requiring a fast data acquisition system. We also present results of the viscosity of a binary gas mixture of methane
and butane from (200 to 423) K and pressures between (10 and 31) MPa along with a comparison with literature values as deviations from the extended corresponding states model implemented in REFPROP 9.1.
The unique properties of ionic liquids (ILs), such as a negligible vapour pressure, high chemical and thermal stabilities, wide liquidus temperature range, and the possibility of fine tuning their properties through appropriate cation/anion combinations make of them viable candidates to replace the common organic and volatile solvents currently used in an extensive range of industrial applications [1]. In fact, there are circa 600 different organic solvents used by industry while there are one million of possible combinations of ions or different ionic liquids [1]. In particular, ionic liquids have been designated as potential solvents for “clean” liquid-liquid extractions [2]. Therefore, the search on novel biphasic systems composed of two ionic liquids, while comprising the determination of their liquid-liquid equilibrium, allows the creation of a new plethora of separation processes constituted only by non-volatile solvents. In this work, immiscible mixtures of cholinium- and phosphonium-based ionic liquids were investigated and their phase diagrams were determined from 40°C to 150°C. Nuclear Magnetic Resonance (NMR) and Electrospray Ionisation - Mass Spectrometry (ESI-MS) were used as analytical techniques for the quantification of each ion/ionic liquid and for the evaluation of the ionic exchange extension in such mixtures.

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References

In proposed processes for carbon capture and sequestration, the captured carbon dioxide will contain some water vapor. When the CO$_2$ is transported in pipelines, it is important to avoid water condensation that can lead to corrosion; optimal design of these systems therefore requires accurate knowledge of the dew point of water in compressed CO$_2$. We have constructed a facility to determine the equilibrium water content at saturation (dew point) in a compressed gas as a function of temperature and pressure. A saturator humidifies the flowing gas by equilibrating it with liquid water at a precisely controlled pressure and temperature. Afterwards, a gravimetric hygrometer measures the water mole fraction of the humid gas. To accomplish this, the hygrometer first separates the water from the gas using desiccants in water collection tubes. Afterwards, it determines the number of moles of collected water (determined from mass measurements of the water collection tubes) and the number of moles of the remaining dry gas. We report dew-point data on six isotherms between 10 °C and 80 °C at pressures from 0.5 MPa to 5 MPa. Analysis of the isotherms indicates that our data are consistent with theoretical estimates by Wheatley and Harvey of the interaction second virial coefficient between H$_2$O and CO$_2$, but our experimentally-determined second virial coefficients have smaller uncertainty. We also experimentally determine estimates for the third virial coefficient corresponding to the interaction between one H$_2$O molecule and two CO$_2$ molecules; no data for this coefficient have previously been reported in this temperature range.
In this contribution, the effects of electrolytes on the phase behaviour of carbon dioxide hydrate forming systems are presented. The phase behaviour of the simple carbon dioxide hydrate system, the mixed carbon dioxide - tetrahydrofuran (THF) hydrate system, and, finally, the effect on the phase behaviour of different overall concentrations of sodium chloride will be elucidated. In addition, the competing effects between THF and an electrolyte of the metal halide series and their impacts on the phase behaviour of the hydrate forming systems will be discussed. The strength of hydrate inhibition by metal halides is compared and, a quantitative analyses between the effect of anions and cations is made in order to gain some understanding on the mechanism of electrolyte inhibition on hydrate formation.
Measurements of thermophysical properties, that is, \( P \rho T \) (pressure - density - temperature) properties, saturated properties, and the critical locus, for several binary and ternary refrigerant mixtures composed of HFOs were made. Our target binary mixtures are the HFO + HFC mixtures, \( R \ 32 + R\ 1234yf \), \( R\ 32 + R\ 1234ze(E) \), \( R\ 1234yf + R\ 1234ze(E) \), \( R\ 134a + R\ 1234yf \), and \( R\ 134a + R\ 1234ze(E) \). And for ternary mixtures, \( R\ 32 + R\ 1234yf + R\ 1234ze(E) \) and \( R\ 134a + R\ 1234yf + R\ 1234ze(E) \) were selected. The experimental results were compared with calculations from REFPROP and the mixing parameters for these mixtures were optimized. In addition, the composition dependence of the critical parameters for these mixtures was also discussed.
Experiment and Analysis on Spectral Properties of Two Kinds of Thermal Radiation Coatings

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Two thermal radiation coatings named Optical Solar Reflectors (OSR) have been measured and analyzed to understand the spectral properties and dependency on temperature. Because of spectral selectivity, the infrared emissivity used for evaluation of radiative heat exchange between this kind of coatings and surroundings, obviously depend on the operating temperature. Based on comparison method, an infrared emissivity experiments device is established, and the corresponding temperature range for the infrared emissivity is from 326 to 426 K. The experimental error for the new device is deduced and the results for the two kinds of sample are dominated. The infrared emissivity for the two sample have lesser difference, and they are both higher than 0.773 at 326 to 426 K. On the other hand, the infrared emissivity doesn't exist linear change along with temperature variation. Moreover, a completed experiment device is employed to obtain the spectral reflectance for the two coating. The typical measurement wavelength for the reflectance is 0.6328, 1.34 and 3.39 micrometer, and the direction hemisphere spectral reflectance is figured out. For the two coatings, the visible light wavelength reflectance is obvious higher than infrared wavelength. In order to analyze the experimental results, a theoretical model is established and the result for 0.6328 micrometer is simulated. Compared the numerical simulation result with the experimental one, the relative error is 4.49%.
Experimental Investigation into Techniques for Reducing Thermal Contact Resistance in Steady-State Thermal Conductivity Measurements

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The National Physical Laboratory (NPL) has developed a new variation on the established guarded hot plate technique for steady-state measurements of thermal conductivity. This new guarded hot plate has been specifically designed for making measurements on specimens with a thickness that is practical for advanced industrial composite materials and applications. During the development of this new guarded hot plate, NPL has carried out an experimental investigation into methods for minimising the thermal contact resistance between the test specimen and the plates of the apparatus. This experimental investigation includes testing of a new approach to specimen surface temperature measurement in the guarded hot plate and also tests on different thermal interface materials for use in another NPL facility based on a commercial guarded heat flow meter apparatus conforming to standard ASTM E1530-11. The results of the investigation include initial validation of the surface temperature measurement in the guarded hot plate through agreement with the thermal conductivity values of NPL reference material. There are also results showing the effect on the measured thermal resistance of applying different quantities of the type of heat transfer paste suggested in ASTM E1530-11 (clause 10.7.3), and the effect on thermal resistance of two alternative types of thermal interface material. One of these alternatives shows improved thermal performance over the heat transfer paste and also has several practical advantages in terms of usability. Acknowledgements: This work was funded through the European Metrology Research Programme (EMRP) Project SIB S2 Thermo. The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.
Reference Correlation of the Thermal Conductivity of \textit{n}-Pentane, \textit{iso}-Pentane, and Cyclopentane from the Triple Point to 700 K and Moderate Pressures

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In this work new, representative reference equations for the thermal conductivity of \textit{n}-pentane, \textit{iso}-pentane and cyclopentane, are presented. The equations are based in part upon a body of experimental data that has been critically assessed for internal consistency and for agreement with theory whenever possible. The thermal conductivity is correlated as a function of the density and the temperature, as a summation of three contributions; a dilute-gas term, a critical contribution term, and a residual term. Densities required are obtained from recent equation-of-state correlations. In the case of the dilute-gas thermal conductivity, a theoretically based correlation was adopted in order to extend the temperature range of the experimental data. Moreover, in the critical region, in addition to a small number of experimental data, the thermal conductivity enhancement is well represented by theoretically based equations containing just one adjustable parameter. The remaining residual contribution is obtaining by empirically fitting critically assessed data. All three correlations are applicable for the temperature range from the triple point of each fluid to 700 K, and an upper pressure limit determined by the maximum density limit for the equation of state used to provide density.
There exists a variety of methods to measure the flow of a liquid through a conduit; however, most of those methods significantly interfere with the flow, which affects the measurement. The use of non-invasive techniques for flow measurement has been developed very little, especially which are based on infrared thermography that has not shown significant improvement. In this work we developed a methodology to measure flow in a conduit, based on thermal images acquired with an infrared camera in the middle infrared range adjusted at ambient characteristics. The experimental setup proposed was studied at external disturbances such as: ambient temperature and humidity, and infrared camera stability in order to find their error contribution during the measurement. To study the sensitivity of the measurement system, we used a flow control capable of causing small changes in this, allowing the measurement of flows with a resolution of milliliters per second with the proposed setup. It is analyzed and discussed how the variations in flow due to changes in temperature or vice versa affect the thermal images acquired, which could lead to an incorrect interpretation of the flow velocity. Additionally, it is discussed how the effects of turbulence produced by curved hoses, and the change in the emissivity of the conduit as a function of the temperature can also affect the measurement.
The transient multi-current hot wire technique is used to determine simultaneously the thermal conductivity ($\lambda$) and thermal diffusivity ($\alpha_T$) of the solid/liquid phase change linear n-alkanes at atmospheric pressure in the range 258-348 K. These compounds are used in Phase Change Materials (PCM) for energy storage and recovery. The same set-up was used to measure $\lambda$ and $\alpha_T$ of the liquid and the solid states at different electrical currents. Both odd- and even-numbered n-alkanes were considered (n-pentadecane, C$_{15}$H$_{32}$, n-hexadecane, C$_{16}$H$_{34}$, n-heptadecane, C$_{17}$H$_{36}$, n-octadecane, C$_{18}$H$_{38}$, n-nonadecane, C$_{19}$H$_{40}$ and n-eicosane, C$_{20}$H$_{42}$). The obtained results were compared with available literature data. In fact, no literature data were found for $\alpha_T$ of the n-alkanes considered in this study. The values obtained for the liquid phase cannot be in any reliable way extended to the solid phase. The discontinuity of $\lambda$ near $T_m$ was found to be higher for the n-alkane having the larger number of carbon atoms. The diffusivity $\alpha_T$ of C$_{16}$, C$_{18}$ and C$_{20}$ is larger in the solid phase than in the liquid phase. Low accuracy for both $\lambda$ and $\alpha_T$ were obtained near (and below) the solid/liquid phase transition of the three n-alkanes, due to the latent heat of melting/crystallization that may affect the temperature of the wire.
The interaction of a hydrated solute with the solvent spans a wide range of energies. Traditionally, in computing the thermodynamic properties of hydration, the problem of disparate energy scales is dealt by alchemically transforming the solute from a non-interacting solute to a fully interacting solute. But at the scale of a globular protein such approaches can prove challenging. Here, guided by the quasichemical organization of the potential distribution theorem, we present an approach that readily applies to systems ranging in complexity from those described by first principles (ab initio) potentials to large molecular solutes such as a protein in water described using empirical (classical) potentials. In this presentation, we will sketch the regularization approach and present results on the hydration thermodynamics in the coil-to-helix transition and in helix-helix pairing of a deca-alanine peptide using classical (empirical) potentials. On this basis, and in contrast to the extant ideas on the role of hydrophobicity in protein folding, we will show that in both the coil-to-helix transformation and in helix-helix pairing, changes in protein intramolecular interactions are decisive in favoring the ordered structure.
Far-from-equilibrium Flow in Nanopores from Molecular Simulation

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Fluids in small nanopores have properties that differ from bulk fluids at the same state point due to the restriction of motion, wall-fluid interactions and layering effects, especially close to the wall. Of particular interest is the change in rheological properties and nonequilibrium flow due to confinement. It has been found that the onset of nonlinear behaviour can occur at lower flow rates when a fluid is confined, and when this occurs linear response theory cannot be applied and the flux will no longer be proportional to the force. We show how nonlinear response theory [1] can be applied to these systems and how it can be used to improve the results obtained from simulations, if nonlinearity sets in at relatively low forcing. Simulations of Poiseuille will be used to demonstrate the behaviour. [2]

Study of lubrication is an area where changes in behavior due to flow is important. In many cases lubrication occurs at high strain rates and under high confinement. In this work we evaluate the response of a fluid under shear flow in a nanopore. The movement of the boundaries in opposite directions induces the shear. The viscous heat generated inside the pore is removed by a thermostat applied exclusively to the atomic walls, leaving the dynamics of the fluid as realistic as possible. [3] We will also discuss the characterization of slip in these small pores.

References

Research on coating is greatly motivated by the emerging need for surfaces with low fouling and biofouling properties, tunable transparency, good anti-icing and improved heat transfer behavior. Approaches to tackle these challenges include superhydrophobic [1,2] or even superamphiphobic [3] surfaces and slippery lubricant infused textured surfaces [4]. In both cases, a deposited drop shows low adhesion to the underlying substrate and rolls or slides off when tilting the surface by a few degrees. In case of superhydrophobic or superamphiphobic surfaces this is achieved by encapsulated air pockets reducing the effective drop-solid contact area, whereas in case of slippery surfaces the encapsulated air is replaced by a lubricant. Until recently, neither quantitative information on the shape of the drop on superhydrophobic or slippery surfaces exists, nor microscopic information on how a drop advances or recedes. In this lecture, I will discuss the possibilities of laser scanning confocal microscopy to monitor the shape of the meniscus and the morphology of the contact lines. As model system we investigated micropillar arrays and inverse opals. Pinning and depinning of the drop from single micropillars is monitored with microsecond resolution, providing first time- and space resolved information on how a drop advances and recedes on a hydrophobic textured surface.

References

Thermal Transport in Deforming Polymers

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The strong coupling of mechanical and thermal effects in polymer processing flows has a significant impact on both the processability and final properties of the material. Simple molecular arguments suggest that Fourier’s law must be generalized to allow for anisotropic thermal conductivity in polymers subjected to deformation. In addition, theoretical results suggest a linear relationship between the thermal conductivity and stress tensors, or a stress-thermal rule. In our laboratory we have developed a novel optical method based on Forced Rayleigh Scattering (FRS) to obtain quantitative measurements of components of the thermal diffusivity tensor in polymers subjected to deformations. We have found the stress-thermal rule to be valid for several polymer systems in both shear and elongational deformations. More recently, we have developed a novel technique based on Infrared Thermography (IRT) that complements FRS and allows for the study of a wider range of polymeric materials. The IRT technique also allows us to investigate the dependence of heat capacity on deformation. These experiments are used to develop an understanding of the molecular origins of anisotropic thermal transport in polymers.
Anyone who has enjoyed a glass of wine has undoubtedly noticed the regular pattern of liquid beads that fall along the inside of the glass commonly referred as ‘tears of wine.’ This fascinating phenomenon is possible only if there is a flow against gravity in the liquid film that forms on the inside of the glass. In 1855, J. Thomson identified the driving force for the upwards flow necessary for the continuous formation of tears as a gradient in interfacial tension, now known as a Marangoni stress. It is generally accepted that the flow leading to wine tears is due to a composition gradient that results from the evaporation of ethanol, which in turn produces an interfacial tension gradient. Here, we revisit the tears of wine phenomenon using a simple hydrodynamic model and a novel experimental technique. Our results demonstrate that the Marangoni force responsible for wine tears is the result of both composition and temperature gradients whose relative contribution depends on the bulk ethanol concentration. The model predicts the range of ethanol concentration for which wine tears are observed, which is strongly influenced by the thermodynamic behavior of ethanol-water mixtures.
Competitive Effects of Chemicals on Hydrate Particle Cohesion

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In oilfield production conditions, many chemicals are present, both in the form of natural surfactants that are present in the oil phase, as well as additives that are injected to control the properties of the oil phase. These additives may include Low Dosage Hydrate Inhibitors (LDHIs) such as Kinetic Hydrate Inhibitors (KHIs) or Anti-Agglomerants (AAs), corrosion or scale inhibitors, dispersants, etc. In order to achieve slurry flow in subsea oil pipelines, the agglomeration of hydrate particles needs to be minimized so that the small, dispersed hydrates are transportable rather than forming larger aggregations that may plug the pipeline. This study focuses on the interactions of several classes of chemicals on the cohesion force between two hydrate particles. A Micromechanical Force apparatus was used to measure the changes in the cohesion force for cyclopentane hydrates when a dispersant, a KHI, and a model AA are added to the cyclopentane phase. The cohesion force is tested for individual chemicals, as well as when multiple chemicals are present. It was found that the interaction of specific chemicals can work synergistically, where the effect is greater than either additive can produce on its own, or antagonistically where the effect is reduced for the chemical mixture, or show no interaction where the cohesion force is similar to when only the more effective chemical is present.
Comparison of Potentiometric and Calorimetric Determination of Standard State Thermodynamic Properties for Ionization of Water up to 573.15 K

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There is a disagreement in the values of the standard state thermodynamic properties for ionization of water calculated from potentiometric [1] and calorimetric measurements [2] at temperatures above 473 K. Accurate standard state (infinite dilution) thermodynamic properties for the ionization of water at high temperatures and pressures are very important in the study of almost all ionic equilibria in aqueous solutions. Because of increasing non-ideality of the electrolytes in even dilute solutions [3], the extrapolated experimental thermodynamic values to standard state (infinite dilution) conditions become more uncertain as the temperature increases. Since ionization of water is perhaps the most important acid-base reaction, it was decided to reinvestigate this disagreement between potentiometric and calorimetric measurements. Using ionic additivity, values for the changes in the standard state Gibbs free energy, enthalpy, entropy, heat capacity, and molar volume for ionization of water, at steam saturated pressure up to the temperature of 573.15 K, are calculated from the recently available corresponding values for the standard state partial molar properties of HCl(aq) [4], NaCl(aq) [5], and NaOH(aq) [6, 7]. Comparison of the present study with the literature data indicate that in fact there are no disagreements between the above mentioned standard state thermodynamic properties for ionization of water calculated from potentiometric and calorimetric measurements. The apparent disagreement is, however, the result of the model chosen to represent the potentiometric data.

References:

New models have been developed to predict the thermophysical properties related to the phase transition of normal alkanes which are the most encountered components in the petroleum industry. The calculations include temperature and enthalpy of solid-liquid (fusion) and order-disorder solid phase transition of pure normal alkanes in addition to the temperature dependency of heat capacity in aforementioned phases as a function of carbon number. For the fusion temperature, 67 experimental data points in the carbon range of 1 to 390 have been used to develop two correlations while 41 experimental data in the carbon range of 1 to 60 have been used to correlate enthalpy of solid-liquid phase transition. Also, 26 experimental data in the carbon range of 9 to 44 have been used to correlate the temperature and another 23 data have been used to obtain the correlation for enthalpy of order-disorder solid phase transition as well as a new model for the estimation of total phase change enthalpy by using the experimental data of fusion and order-disorder solid phase transition. Due to the difference of heat capacity in the liquid, disorder solid and order solid, three heat capacity models have been presented based on the group contribution approach for a wide range of carbon number as a function of temperature according to the available experimental data. Average absolute deviation percent (AAD %) of the new models has been obtained 0.66, 3.47, 0.35, 4.09, 7.52, 0.54, 4.65 and 6.89 for fusion temperature, fusion enthalpy, order-disorder solid phase transition temperature, order-disorder solid phase transition enthalpy, total phase change enthalpy, heat capacity in liquid, disorder and order solid phase, respectively, by more than 1300 experimental data points. The results demonstrate that these new approaches are in more agreement with experimental data in comparison with the other methods presented in the literature.
Measurement and Evaluation of Apparent and True Thermophysical Properties of Materials during Phase, Chemical, and Structural Transformation

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The peculiarities of many materials during heating at the wide temperature range are chemical, phase and structural transformations accompanied by latent heat effects. The main problems in investigation of thermal physical properties of these materials can be formulated as follows:

· How to measure apparent thermophysical prosperities during chemical, phase and structural transformations;

· How to determine true thermal physical properties required for heat and mass transfer calculations during chemical, phase and structural transformations.

The problem in experimental measurements of thermophysical properties is the impossibility of using steady state methods during time-dependent physical and chemical processes in the materials. Using of transient methods, for example hot wire or laser flash methods, is also incorrect, since the measurement process has to be started only after steady state temperature field is established in the sample, i.e. when the processes could be finished. The best way to measure thermal physical properties during the processes is measuring during monotonic heating which can be a model of real technology. These methods are applied widely for test of specific heat based on DSC analyses. The special standard ASTM E2584 was developed for apparent thermal conductivity measuring during monotonous heating/cooling.

We discuss in this paper some limitation of the standard methods and describe novel methods and technique for measurement of thermal diffusivity, thermal conductivity, and specific heat during monotonous heating of the sample. Determination of true thermal physical properties is based on excluding of latent heat effects and modeling of apparent thermal conductivity and heat transfer mechanisms.

Thermal diffusivity and specific heat of materials with different composition and density (ceramics, gypsum, and minerals) were measured in this work in the temperature up to 1700°C. True thermal conductivity was determined as a product of the measured thermal diffusivity, volume specific heat in which latent heat effect were excluded.
Measurement and Evaluation of Apparent and True Thermophysical Properties of Materials during Phase, Chemical, and Structural Transformation

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New VLE and Calorimetric Data for Binary Mixtures of Light Hydrocarbons, and Stringent Tests of Equations of State at Low Temperatures and High Pressures

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New $PT\text{xy}$ data are reported for binary mixtures of methane + ethane, methane + propane, methane + 2-methylpropane, and methane + butane over a temperature range from (203 to 273) K at pressures up to 9 MPa. Isobaric heat capacity data are reported for liquid mixtures of methane + propane and methane + butane at pressures between (4.7 and 6) MPa and temperatures between (108 and 178) K. The VLE measurements help identify the literature data sets which are erroneous or have relatively large uncertainties but are still frequently included in the development of new equations of state. The new data are compared with both the GERG-2008 and Peng Robinson EOS as implemented in commercial process simulation software. While the multi-parameter EOS generally describes the VLE data more accurately than the cubic EOS as the critical region is approached, there are important cases such as CH\textsubscript{4} + C\textsubscript{4}H\textsubscript{10} at 244 K where the simpler EOS is significantly more accurate. When compared with the mixture heat capacity measurements, the GERG EOS predictions were generally within (2 to 5) % of the data, whereas the Peng-Robinson EOS predictions deviated by around 10 %. However, when extrapolated to 118 K and butane mole fractions of 0.4, the deviations in the mixture heat capacities predicted by two EOS increased to 110 % and 21 % for the GERG and cubic EOS, respectively. These comparisons also suggest a method of identifying measurement conditions where new experimental data would be most valuable.
Gas Hydrate Wall Film Growth as a Precursor to Pipeline Blockage

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In subsea oil and gas pipelines, high-pressure reservoir fluids will cool upon exposure to the cool subsea environment. At low temperature, small hydrocarbon molecules (e.g. methane) and liquid water will react to form gas hydrate particles, which may fully occlude and block the pipeline. Conventional management strategies focus on complete avoidance of hydrate by removing the pipeline’s conditions out of the hydrate stability zone. In deep-water systems, this avoidance strategy may be economically unviable. In order to move toward a hydrate management strategy, the mechanism of hydrate blockage formation must be well characterised. Limited studies have suggested a hydrate film may form on the pipeline wall early in hydrate blockage formation, but this phenomenon has not been directly observed to date. This study introduces a new suite of high-pressure sapphire autoclave experiments, where gas hydrate plugs were formed over a range of watercut (10-100 vol% of the liquid phase) and hydrate inhibitor (0-30 wt% monoethylene glycol) conditions. Visual observation of the sapphire cell informs a new conceptual picture for hydrate blockage formation, where initial hydrate nucleation is consistently proceeded by the formation of a hydrate film at the wall. The growth and annealing rate of this film was found to depend on both hydrate guest availability and the driving force for growth. The film plays a critical role in enabling the formation of a moving hydrate bed at the gas-water or oil-water interface, and the deposition of solid hydrate particles or aggregates in the latter stages of hydrate plug formation. This data informs a new approach to hydrate management strategies, where the prevention of hydrate film formation, as opposed to complete prevention, may enable a transportable slurry with a controlled hydrate volume fraction.
Computation for Pressure of Condensation of Hydrocarbon Mixtures

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We study the main characteristics of gas condensate deposit considering that product extracted on the surface, gas and condensate in stratal conditions, is in quasi-single state. It is assumed that extracted gas condensate system in stratal conditions is presented as the gas phase and its pressure at stratal temperature corresponds to stratal pressure. We consider information on phase transition of gas-condensate systems taking into account pressure values of single-phase state where system properties depend on its composition. In gas condensate deposits the hydrocarbon systems are in the near critical states. The thermodynamic behaviour of their product is considered regarding phenomena of retrograde evaporation and retrograde condensation and is based on the laws of phase equilibrium of binary and multicomponent hydrocarbon systems. For development of computational method the multiform gas condensate systems have been generalized on the base of the following parameters: average molecular mass of entire system, weight-average reduced molecular mass and stratal temperature. The pressure of single-phase state is the function of given parameters. Average molecular mass of hydrocarbon system considers light and medium components, as their content is prevailing. Weight-average reduced molecular mass includes heavy components. Hydrocarbon mixture contains significant quantity of given components and considerably influences the pressure of single-phase state. Regarding the experimental data, we obtained the equation to find the pressure of initial condensation of single-phase state of hydrocarbon systems. Using this equation, we calculated the pressure of single-phase state. Offered computational method for pressure of single-phase state systems can be used for prognosis of oil gas condensate systems and for compilation of reference data on thermophysical properties of hydrocarbon mixtures of various deposits.
A New Viscosity-Surface Correlation for Propane

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The exact knowledge of thermophysical properties of fluids with industrial importance is needed for a more accurate basic design of compressors, gas turbines, and gas pipelines. In contrast to thermodynamic properties, transport properties of propane, particularly in the region near to the critical point, are not sufficiently well known. The current NIST standard data base REFPROP 9.1 of Lemmon et al. (2013) recommends the viscosity correlation of Vogel et al. (1998), which is characterized by uncertainties of ±(2.5-4)\% in their range of validity. This viscosity-surface correlation was based on an outdated equation of state of Younglove and Ely from 1987, whereas REFPROP 9.1 recommends the reference equation of state of Lemmon et al. (2009) for thermodynamic properties of propane.

Recently, new very accurate viscosity measurements were performed by Seibt et al. (2011) using a vibrating-wire viscometer combined with a single-sinker densimeter. The uncertainty of these data was conservatively estimated to be ±(0.25-0.4)\%, increasing with temperature. Consequently, they are considered to be primary data. In addition, viscosity measurements by Wilhelm et al. (2001) were re-evaluated (2011) and have to be considered as primary data, too.

Based on the new reference equation of state and on the improved data situation in the dense-gas region, a new viscosity-surface correlation for propane was generated using the structure-optimisation method by Setzmann and Wagner (1989). The bank of terms comprises expressions for different regions: the limit of zero density, the higher-density fluid region, and the near-critical range. Calculated values using the new viscosity-surface correlation were compared with the primary data sets, which were used in the development of the correlation. In addition, the correlated values were compared with values resulting from the earlier viscosity-surface correlations of Vogel et al. (1998) and of Scalabrin et al. (2006).
Nosé-Hoover NVT molecular dynamics (MD) was applied to study stability of molecular phases of solid nitrogen at high pressures. Molecules forming the solid were considered as non-rigid strongly bound pairs of atoms. Intermolecular interaction was represented by the sum atom-atom and quadrupolar forces. We have determined the pressure dependence of melting temperature of highly compressed solid nitrogen and examined the influence of the quadrupole interaction on the stability of different solid phases. Results of two types of MD simulations: single-phase and two-phase in the box were compared. We observed turnover of the melting temperature at megabar pressure and discuss its possible explanations. Location of the vibration-rotation transitions between cubic phases in the solid nitrogen were located by monitoring the character of the orientational motion of molecules. The potential model reproduces the properties of dense solid nitrogen and the transition lines between orientationally ordered and disordered high pressure phases. It was found that quadrupolar forces have only a weak influence on the structure, energy and pressure, but significantly affect the stability of the crystalline structures and the location of the melting and orientational transitions on the phase diagram of nitrogen. The study of transitions between phases having different symmetry of crystalline lattice is a serious problem for MD simulation technique. We propose a method to solve this problem which combines MD simulation and theoretical equations of state. The efficiency of this method is demonstrated on prediction of the transition line between FCC and HCP phases at high pressures.
Density Measurements under Pressure for the Binary System Di-Butyl Ether + 1-Heptanol at Temperatures up to 393.15 K and at Pressures up to 140 MPa.

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The increasing worldwide use of bio-fuels constitutes one of the measures considered to reduce greenhouse gas emissions. Bio-fuels also have an important part to play in promoting the security of energy supply, and promoting technological development and innovation. Di-butyl ether (DBE) is used as blending agent in reformulated gasoline and has been included in recent international regulations on the promotion of the use of energy from renewable sources for transport. The DBE acts as non-polluting, high octane number blending agent. DBE could be also used as cetane enhancer in bio-diesel fuel, and can be obtained as an added valued additive to second generation bio-fuels. Ether + alcohol mixtures are of interest as model mixtures for gasoline in which the ether and the alcohol act as non-polluting, high octane number blending agents. Despite of this interest, density data of binary mixtures containing ether + alcohol at pressures other than the atmospheric pressure are very scarce in the literature. Density of the binary mixture DBE + 1-heptanol have been measured under pressure and reported in this work using a vibrating tube densimeter. Experimental densities for the binary system DBE + 1-heptanol have been measured at 298.15, 313.15, 333.15, 353.15, 373.15 and 393.15 K and at twenty-three isobars up to 140 MPa. For each composition, the experimental values were correlated using a Tait-type equation. Furthermore, the excess molar volume and the isothermal compressibility were calculated from the density data. The authors acknowledge support for this research to the Ministerio de Ciencia e Innovación, Spain, Project and ENE2009-14644-C02-02.
Viscosity of ionic liquids (ILs) varies from low-viscosity fluids, similar to common organic solvents, to glasslike extremely viscous fluids. This property depends strongly on the molecular structure and is highly dependent on the interactions between the ions: electrostatic, van der Waals interactions and hydrogen bonding. We have analysed the effect of the structure on the viscosity and its temperature dependence [1,2]. Despite of the large amount of studies of viscosity of ILs at atmospheric pressure, viscosity database of these fluids at high pressure is still scarce [3-4]. In this work we present viscosity measurements for eight ILs performed by means of a falling-body viscometer at several temperatures and at pressures up to 150 MPa. The cations of these ILs are of pyrrolidinium and imidazolium types whereas the anions are triflate, ethylsulfate and other imide and phosphate derivatives. Experimental data were used to check the application of the thermodynamic scaling approach as well as the hard-sphere scheme to these ILs. Furthermore, the film forming capability for elastohydrodynamic lubrication of these liquids was evaluated and compared with those of other lubricants.

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References

The Solubility of Hydrogen Sulfide and Carbon Dioxide in Propylene Carbonate

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Over the years, a number of techniques have been proposed to remove acid gas components (H₂S and CO₂) from gas streams. One technique is to use propylene carbonate to strip these components from the gas stream. There is a large amount of published solubility data for carbon dioxide and hydrogen sulfide in these solvents and the development and validation of any vapor-liquid equilibrium model requires a thorough knowledge and review of the available data. With this in mind, an exhaustive review of the solubility data of hydrogen sulfide and carbon dioxide in propylene carbonate available in the literature was performed. To complement and extend the existing data set, new measurements of the solubility of hydrogen sulfide in propylene carbonate were performed.

All of the available data for the binary systems (H₂S + propylene carbonate) and (CO₂ + propylene carbonate) were correlated with the Peng-Robinson equation of state and values of the binary interaction parameters were obtained. Using the expressions relating the binary interaction parameters with the parameters of the Krichevsky-Illinskaya equation, Henry's coefficients for the solutes in propylene carbonate were calculated. The new data and the modeling results will be compared with the previously reported Henry's law coefficients. Comments on the individual data sets and recommendations for future measurements will be made.
In this paper, Pulse Phase Thermography (PPT) and other processing techniques will be presented in the context of IR Thermography NDE. It is recalled PPT was proposed in 1996 as a new mean to look at thermographic data obtained from pulsed experiments. Up to that time, two stimulation approaches were common for thermographic NDT. Pulsed thermography (PT) which consists in flash-heating specimens and lockin thermography (LT) which consists in modulated heating. In PT, images were generally processed in the time domain by mean of a basic thermal contrast. Such temperature differences observed on the specimen surface corresponds to how well or not the heat flow propagates within the bulk of the specimen. A subsurface defect acts as a thermal barrier, hence the «heat accumulates» just over it translating as a higher surface temperature. In LT, the images were processed in the phase domain. Phase is related to the propagation delay of the thermal waves propagating into the specimens. A careful choice of the stimulation modulated frequency yields to thermal waves propagating at the depth corresponding to possible defects (for example the glue line in a laminate). By analyzing the PT data in the frequency domain thanks to the Fourier transform, PPT enabled PT data to be analyzed as LT data and thus unified somehow these two approaches. Moreover, such analysis enhanced significantly the results by reducing the noise (optical heating and infrared effects). As stated above, before PPT, the main processing technique was the basic «thermal contrast». After the release of PPT, others processing techniques have emerged as well such as TSR (Thermographic Signal Reconstruction), PCT (Principal Component Thermography), and more recently PLST (Partial Least Square Thermography). Since then, these techniques have been adopted by the community and are common tools nowadays however, it is difficult to evaluate them quantitatively in a particular context. In this paper, these techniques will be presented and their capabilities will be compared using a newly developed quantitative tool.
Au-Water Nanofluid:  
Experimental Measurements and Numerical Simulation of the Yearly Yield  
of a Parabolic Trough Collector

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In recent years, nanofluids, i.e. dispersions of solid particles into common fluids, have been studied to enhance the efficiency and performance of the solar thermal systems due to their enhanced thermophysical properties. In this work, thermal conductivity and dynamic viscosity of a water based gold nanofluid were measured and the nanoparticle stability was investigated. Experimental data were used as input for a numerical simulation to analyze the effects of nanofluids on the performance of a parabolic trough solar collector (PTC). Here, a direct comparison with the base fluid is provided in order to prove the convenience in the adoption of nanofluid as energy media.
The estimation of the second virial coefficient is generally based on the corresponding states principle and takes into account semiempirical correlating methods that are usually valid only for nonpolar gases or small polar molecules. Thus, in this work we present a correlation of the second virial coefficient valid for organic and inorganic compounds. Firstly, we statistically analyzed more than 6000 experimental points collected from literature. The data was deeply investigated with a factor analysis approach in order to identify the most significant parameters that influence the second virial coefficient. The factor analysis, combined with physical considerations, allowed us to find a simple equation that gives lower deviations with respect of those available in literature. Furthermore, we built the architecture of an artificial neural network to improve the prediction capability of the second virial coefficient; in particular, we used a multi-layer perceptron with a single hidden layer. We trained, validated, and tested several configurations of the neural network in order to obtain the number of neurons in the hidden layer that minimizes the deviations between experimental and calculated points. Results show that the artificial neural network is able to predict the second virial coefficient with greater accuracy than that of correlations available in literature.
Non-equilibrium Molecular Self-Assembly

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Self-assembled structures such as micelles and vesicles have frequently been discussed as model systems for biological cells because they can mimic their ability to compartmentalize matter for biological and material processing such as DNA-replication and nanoparticle synthesis respectively. However, in contrast to most synthetic self-assembling systems the natural systems are not equilibrium processes. Attention is therefore now focusing on non-equilibrium self-assembling systems where energy input is required to sustain the self-assembled state. These systems have the potential to adapt themselves and enter into different self-assembled states depending on environmental conditions whereas their equilibrium counterparts can only assemble or disassemble. Recently, such a self-assembling system using a chemical fuel[1] and presently more examples are being worked on. The thermodynamic description of such non-equilibrium processes[2] invokes some interesting questions regarding the nature of the entropy production, the relation between the driving forces and the dissipation rate, and the energy transduction pathways. In particular, an interesting question is whether multiple stationary states can be found in such systems and this will be discussed during this presentation.

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The electrolysis of molten salts containing rare earth chlorides has been widely used for production of rare earth metals and their alloys. Information about the surface tension of molten salts is essential for understanding the structure of the systems and for upgrading the technology of the electrolytic production of rare earth metals. In this paper, the method for calculating the surface tension of molten salts containing rare earth chlorides based on Butler’s original treatment was described. A new approach to estimating the partial excess Gibbs energy in the surface phase of molten salts using thermodynamic data obtained from the CALPHAD (calculation of phase diagram) technology in the bulk phase was proposed in order to improve the accuracy and applicability of the above method for surface tension calculation. Model parameters are dependent on temperature and composition of molten salts in our treatment, which are supposed to be more reasonable in contrast to earlier work. As examples for illustration, surface tensions of molten salts ReCl$_3$-ACl (Re=Y, La, Ce, Pr; A=Na, K) were calculated using the method proposed in the present work. The calculations of surface tension of LaCl$_3$-ACl (A=Na, K) systems from our method agree better with the experimental data than those from the method in previous work. It’s believed that our method has better applicability for predicting the surface tensions of various molten salts containing rare earth halides.
Experimental Measurement of Thermophysical Properties of H$_2$O/KCOOH Desiccant

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The sorption dehumidification of air by desiccant is an interesting alternative to the traditional dehumidification process of cooling the air below the dew point. Desiccant includes liquid, such as hygroscopic salt or glycol solution, and solid, such as silica gel, zeolites or activated alumina. The hygroscopic salt solutions currently used as desiccant are H$_2$O/LiCl and H$_2$O/LiBr which ensure very effective dehumidification performance, although they are corrosive and very expensive. The new hygroscopic salt solution H$_2$O/KCOOH is cheap, non-corrosive, biodegradable, and it exhibits a very high solubility (up to 80% at ambient temperature) which ensures a consistent humidity reduction, therefore it seems to be very promising as "desiccant of the future". H$_2$O/KCOOH is currently used at low salt concentration as heat transfer medium and biodegradable de-icing solution and its thermophysical properties are available only for concentration in salt from 20 to 40%, not interesting for desiccant application. Therefore there is a specific need for a sound amount of new experimental data on thermophysical properties of H$_2$O/KCOOH solution in the typical concentration and temperature range for desiccant application.

The aim of this paper is to measure the thermal conductivity and the dynamic viscosity of H$_2$O/KCOOH solution with a concentration in salt from 60 to 80% in the temperature range from 0 to 80°C. The thermal conductivity measurement were performed by using a Transient Hot Disk TPS 2500S apparatus instrumented with the 7577 probe (2.001 mm in radius) having a maximum uncertainty ($k=2$) within ± 5.0%. The rheological analysis and the dynamic viscosity measurement were carried out by a rotating disc type rheometer Haake Mars II instrumented with a double cones probe (60 mm in diameter) having a maximum uncertainty ($k=2$) within ± 5.0%. The experimental measurements were compared both with other experimental measurements available in the open literature and theoretical models for thermophysical properties of hygroscopic salt solutions.
The excluded volume theory of lattice fluids (introduced in Fluid Phase Equilibrium 372 (2014) 126-140) is enhanced by specifying models for both the attractive and repulsive interaction energy terms. This results in an interaction energy function exhibiting a potential well reminiscent of a generalized Lennard-Jones potential. However here the potential well is seen in the Gibbs free energy function at the macro level. It improves the ability of the model to correlate saturated liquid density. The success of this theory is based on the following ideas: (1) Intramolecular and intermolecular bonds can be treated as uncorrelated when modeling the partition function. The method used to separate the bonds, which is based on an application of Bayes’ theorem, makes a chain molecule appear to have only one segment in a lattice in which the intramolecular bonds are excluded. (2) The attractive forces active between molecules are thought of as being resolved along the generating lines of an assumed lattice. Resolution of these forces along lattice generating lines results in intermolecular bonds i.e. interaction bonds. The energy in an interaction bond is assumed to be inversely proportional to some power of the separation distance between molecules along the lattice line connecting the two molecules. This results in an interaction potential expressed as a polylogarithm with an argument given by a function of the ratio of density to maximum density. (3) An entropic based repulsive force is introduced that opposes the attractive forces. The repulsive force is assumed to be inversely related to the number of configurations available to a molecule in the lattice. Increasing the available configurations decreases the repulsive component of the interaction energy. (4) Strong energetic effects can be modeled based on a random occupation of lattice sites. For example if the attractive forces between molecules is strong enough to cause clustering the molecular cluster is assumed to randomly occupy lattice sites. The improved model is successfully applied to the vapor liquid equilibrium of ethane, ammonia and water, and to the binary mixtures of propane-butane and R152a-butane.
There have been conflicting statements in the literature of the last twenty years about the behavior of the apparent thermal conductivity of two- or three-phase systems comprising solid particles with nanometer dimensions suspended in fluids. It has been a feature of much of the work that these multi-phase systems have been treated as if a single-phase fluid and that the thermodynamic characteristics of the system have varied even though the systems have been given the same name. These so-called nanofluids have been the subject of a large number of investigations by a variety of different experimental techniques. In a recent paper, we critically evaluated the studies of seven of the simplest particulate/fluid systems; Cu, CuO, Al2O3, and TiO2 suspended in water and ethylene glycol. Our conclusion was that when results for exactly the same thermodynamic system, are obtained with proven experimental techniques, the apparent thermal conductivity of the nanofluid exhibits no behavior that is unexpected and inconsistent with a simple model of conduction in stationary, multiphase systems [1]. The wider variety of behavior that has been reported in the literature for these systems is therefore attributed to ill-characterization of the thermodynamic system and/or the application of experimental techniques of unproven validity.

In this work the enhancement of the apparent thermal conductivity of water or ethylene glycol when multi-wall (MWCNT) or double-wall carbon nanotubes (DWCNT) are added to the liquid phase, is investigated. These systems differ from those containing near spherical particles because solid/solid contact and extended conductive pathways in the solid are much more important. The aim is to examine whether the wide variety of behavior that has been reported in the literature for these systems has also to be attributed to ill-characterization of the thermodynamic system and/or the application of experimental techniques of unproven validity, or whether the heat transport processes are genuinely different in different geometries and on different timescales as might be expected from this particular kind of multiphase system.

References

Methodologies to Obtain the Isobaric Thermal Expansions for Simple Fluids and Biodiesels

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In the quest for efficient, reliable and abundant low-cost automotive fuels, knowledge of thermophysical properties of new fuels is of paramount importance in applications, e.g. for the design of engine injectors to be used at higher temperatures and pressures as well as in fundamental research focusing on developing models for an accurate thermodynamic description of such fuels. Due to the importance of the isobaric thermal expansion \( \alpha_p \) in engineering applications, in this work we used two methods for determining \( \alpha_p \) of simple liquids (toluene and 1-butanol) and two biodiesels (obtained from wasted oils). The experimental techniques used were an automated vibrating tube densimeter \([1]\) measuring densities with an uncertainty of ± 0.2% at temperatures up to 423 K and pressures up to 140 MPa and a scanning transitiometer \([2]\) to directly determine \( \alpha_p \) with an estimated uncertainty of ±2% through temperature scans in the range (273 to 423) K and pressure scans up to 170 MPa. From the experimental densities \( \rho \) may be obtained either numerically or by differentiating, with respect to temperature, appropriate analytical equations correlating the densities. However, we note that in the case of the biodiesels \( \alpha_p \) cannot be obtained with good precision by using the Tammann-Tait equation. The methods used in this work permit a satisfactory check of the internal consistency of the different experimental techniques and data reduction for different types of fluids. Comparing the experimental results obtained via transitiometry with those determined via density measurements, differences of about 5% are found. This indicates that the \( \alpha_p \) data determined indirectly from densities are in overall good agreement with the data measured directly by transitiometry. Typically, the single crossing region of isotherms of the isobaric thermal expansion plotted as functions of pressure is satisfactorily reproduced with both methods.

References

Molecular Simulation of Thermodynamic and Transport Properties for the $\text{H}_2\text{O}+\text{CO}_2+\text{NaCl}$ System

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Thermodynamic and transport properties of $\text{H}_2\text{O}+\text{NaCl}$, $\text{H}_2\text{O}+\text{CO}_2$, and $\text{H}_2\text{O}+\text{CO}_2+\text{NaCl}$ mixtures were studied by Monte Carlo and molecular dynamics simulations. For the binary mixture $\text{H}_2\text{O}+\text{NaCl}$, the vapor pressure, liquid densities, viscosities and liquid-vapor interfacial tensions were obtained. For the binary mixture $\text{H}_2\text{O}+\text{CO}_2$ and the ternary mixture $\text{H}_2\text{O}+\text{CO}_2+\text{NaCl}$, the $\text{CO}_2$ solubilities in $\text{H}_2\text{O}$-rich and $\text{CO}_2$-rich phases as well as $\text{CO}_2$ and $\text{H}_2\text{O}$ diffusivities were obtained. Two sets of recently proposed Drude oscillator based polarizable force field models were studied and compared with several fixed-point-charge non-polarizable models. [1, 2] These models use either Lennard-Jones 12-6 or Buckingham exponential-6 functional forms to describe the short range interactions, while the long-range Coulombic interactions were modeled by point charges or Gaussian charges. In particular, for polarizable models, the SWM4-NDP [3] and BK3[4] water models, and the AHNDP [5] and BK3 [6] ion models were studied. For fixed-point-charge non-polarizable models, several existing models for H2O (SPC, SPC/E, Exp-6 [7] and TIP4P/2005), CO2 (EPM2 and TraPPE), and ions (Smith-Dang, Joung-Cheatham and Tosi-Fumi) were investigated. It was found that none of the non-polarizable models was able to produce simultaneously all properties of interest.

References

The Kubo formula for the thermal conductivity of per stratum of few-layer graphene, up to five, are analytically calculated within the tight-binding Hamiltonian model and Green's function technique, compared with the single layer one. The results show that by increasing the layers of the graphene, this conductivity decreases. Although, the change in its magnitude varies less as the layer number increases to beyond two. This could be explained by overlapping of the normal oriented non-hybridized pz orbital. So that in analogy with isolated single layer, these inter-layer interactions provide new vertical channels for moving electrons and distract a fraction of their motivation from horizontal traces parallel to the layers, towards new built-in perpendicular tracks. In other words, overlapped on-hybridized pz orbital gives rise to a partial deviation of the electrons' mobility from the planes for the sake of upright directions. The consequence of these inter-layer possibilities of movement would be a reduction in the intra-layer displacements, and hence, a decay in the flake thermal conductivity. This phenomenon is of more significance as the number of the layers increases, rationally compatible with the last argument, because adding more layers generates more detour paths for electrons, so the plane components of motion will bear a decline.
Transport properties of transformer oil are important parameters for electric equipment designing. In this work, specific heat capacity of transformer oil was measured from 253K to 353K using flow calorimetry. At the same time, influence of transformer oil’s specific heat capacity was investigated. The specific heat capacity of transformer oil increases linearly with temperature increasing. Above all, specific heat capacity of transformer oil is seldom influenced by refining depth and additives, while mainly affected by hydrocarbon composition. Different hydrocarbons have different effect on the specific heat capacity, and the order is alkanes; hydrocarbon composition; specific heat capacity; viscosity; flow calorimetry.
An Experimental Investigation of Oscillation Characteristics and the Heat Transfer Performance of Closed-Loop PHPs with Large Inner Diameter

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The pulsating heat pipe is an increasingly promising device in the application of the electronic cooling due to its obvious advantages—simple structure, low cost and effective heat transfer capability. A series of experiments were performed to investigate the oscillation characteristics and the heat transfer performance of closed-loop PHPs charged with deionized water under different inner diameters (1mm, 2 mm, 3 mm, 4 mm), heat input (20W-90W) and charging ratios (30%-70%). In the experiments, the closed-loop pulsating heat pipe was vertically placed and the bottom section was heated. According to the present study, when other conditions remain unchanged, the closed-loop PHPs with larger inner diameter appear to have not only larger heat transfer capacity and smaller thermal resistance, but more demand of heat input and of longer time to start and oscillate steadily, comparing to the smaller ones. By changing the pipe diameter and charging ratio, dryout characteristic of the pulsating heat pipe was measured by increasing heat input (50-120 w) steadily. The dryout characteristics of PHPs with different inner diameters and different charging ratios were compared, and the influence to dryout characteristic of PHPs will be summarized.
Boronic acids have been found to be important in a variety of biological and medial processes. Phenylboronic acid in particular is used to treat fungus bacterial infections. The literature has a lack of thermo-physical data on aqueous solutions of phenylboronic acid and water soluble derivatives. In this work, the densities and sound velocities of phenylboronic acid in water were measured as a function of temperature ranging from 288 K to 323 K (15°C to 50°C) with 5 K intervals at selected molalities using DMA 5000 M PAAR Density and Sound Meter with an uncertainty of ± 5 x 10⁻⁶ g/cm³ and ± 5 x 10⁻¹ m/s. Apparent molar volumes (Vφ) and apparent molar adiabatic compressibility (Kφ,s) were determined from the obtained experimental data. Partial molar volumes (V_m) and partial molar isentropic compressibilities (K^0_φ,s) at infinite dilution were calculated from the corresponding data. Furthermore, the partial molar expansivity (E^0) and Hepler’s constant were calculated. The parameters were interpreted in terms of solute-solvent interactions, solute-solute interactions, and structure making/breaking behavior of phenylboronic acid in water. Positive partial molar expansivity and Hepler’s constant for the solutions indicate that phenylboronic acid is a structure making solute in aqueous solution.
The densities and sound velocities of trans-resveratrol in ethanol were measured as a function of temperature ranging from 288 K to 323 K (15°C to 50°C) with 5 K intervals at selected molalities. Apparent molar volumes ($V_\phi$) and apparent molar adiabatic compressibility ($K_{\phi,s}$) were determined from the obtained experimental data. Partial molar volumes ($V_m$) and partial molar isentropic compressibilities ($K_{0,s}$) at infinite dilution were calculated from the corresponding data. Furthermore, the partial molar expansivity ($\xi_0$) and Hepler’s constant were calculated. The parameters were interpreted in terms of solute-solvent interactions, solute-solute interactions, and structure making/breaking behavior of trans-resveratrol in ethanol. Analyses show that trans-resveratrol in ethanol solution has strong solute-solvent interactions, weak solute-solute interactions, and that trans-resveratrol behaves as a structure breaking solute.
Near-Field Thermodynamics and Energy Harvesting

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We show that the maximum work that can be obtained from the thermal radiation emitted between two planar sources in the near-field regime is much larger than that corresponding to the blackbody limit [1]. This quantity as well as an upper bound for the efficiency of the process are computed from the formulation of thermodynamics in the near-field regime. The case when the difference of temperatures of the hot source and the environment is small—relevant for energy harvesting—is studied in detail. We also show that the thermal radiation energy conversion can be more efficient in the near-field regime [1]. These results open new possibilities for the design of energy converters that can be used to harvest energy from sources of moderate temperature at the nanoscale.

References

Current Spikes Due to Phase Transitions at Electrode-Electrolyte Interfaces: Effects of Finite Size and Surface Inhomogeneity

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We present a statistical mechanical description of the current spikes associated with first-order phase transitions exhibited during under potential deposition (UPD). The latter is a phenomenon in which a metal ion is deposited on a more noble metal electrode, thus resulting in monolayer (or just a submonolayer) deposition. If such a deposition is sudden, within a narrow voltage range, it is reflected in the current versus voltage plot as a sharp spike and can be interpreted as a first-order phase transition at the electrode-electrolyte interface. Using 2D lattice gases to model UPD processes, it turns out that a current spike resulting from a single crystalline domain (representing an electrode surface) is much taller and sharper than an experimental spike. Our key idea is to use the fact that real electrode surfaces are not monocrystalline but composed of a large number of finite crystalline domains. Therefore, we consider the currents from all domains and interpret an experimental spike as a sum of the domain spikes. Since the domains are energetically inhomogeneous and of different sizes, the domain spikes are mutually shifted and of different heights and widths. Consequently, their sum can produce a spike that is much smaller and broader than the one from a single domain and can be successfully used to model an experimental spike. We apply our results to fit the experimental current spikes for the UPD of Cu on the (111) surface of a Pt and an Au electrode.
Water is arguably the most important molecule on Earth, with a near ubiquitous role in biological, chemical and industrial processes. Despite its molecular simplicity, accurately predicting its properties, which involves many known examples of anomalous behavior, has been surprisingly difficult. Historically, attempts to predict its behavior were confined largely to either empirical correlations or equation of state modelling [1], [2]. More recently, molecular simulation [3] has become the method of choice because of the nexus between underlying intermolecular interactions and observable macroscopic properties. An accurate intermolecular potential for the evaluation of inter-particle forces or energies is the key to reliable predictions. Many alternative intermolecular potentials for water [4] have been proposed, although the basis of the underlying model is often largely semi-empirical. The most widely used models are rigid and variants of either the four-site transferable interaction potential (TIP4P) or the three-site simple point charge (SPC, SPC/E) models. These types of potentials are computationally easy to implement and in many cases they have provided worthwhile predictions. Comparisons with experimental data are often focused at relatively low temperatures and pressures, with a temperature of 25 ºC and a pressure of 1 atmosphere being a popular choice. Polarization is a very important contribution to the intermolecular interaction in water that has been largely missing from many simple potentials. Recent work [5], using an ab initio based potential (MCYna) strongly indicates that including polarization greatly improves the accuracy of predictions. In this work, we report molecular dynamics results for phase equilibria, thermodynamic properties and diffusion data for both water and aqueous mixtures using the MCYna potential, other alternative polarizable potentials, and traditional potentials such as TIP4P/2005, SPC and SPC/E. The comparison with experimental data covers a wide range of temperatures and pressures. It is demonstrated that, in many cases, including polarization in the MCYna potential results in almost perfect agreement with experiment and as such it is more accurate than can be obtained from conventional approaches. Importantly, the improvement gained in accuracy was achieved without resorting to fitting theory to experiment and as such the calculations represent genuine a priori predictions.

References

We propose an extension of Onsager’s theory, originally formulated to describe non-equilibrium aged systems, in order to analyze the dynamics systems characterized by degrees of freedom that relax in different time scales (aging). Our theory is based on the assumption of local quasi-equilibrium states in phase space having a non-stationary probability density. This assumption entails the existence of a time-dependent temperature of the system $T(t)$ reflecting lack of thermal equilibrium between system and bath, which enables us to formulate a Gibbs equation. The relation between the local quasi-equilibrium and bath temperatures is given in terms of a scale function. We show that the fluctuation-dissipation relation remains valid in terms of the local quasi-equilibrium temperature $T(t)$ of the system whose value depends on the timescale considered. The formalism is applied to systems with a slow relaxation dynamics and to granular systems.
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The EPI Suite™ (Estimation Programs Interface) is arguably the most comprehensive freeware for estimation and storage of physical/chemical property and environmental fate estimation data. A part of the suite is program HENRYWIN™ that provides the Henry’s law constant at 25°C and 1 bar from experimental database, if available, and using the group contribution and the bond contribution estimation methods. The purpose of this paper is the extension of the EPI bond contribution method to thermodynamic properties that are derivatives of the Henry’s law constant: partial molar volume, hydration heat capacity and hydration enthalpy. Using simple thermodynamic integration, these properties allow reliable estimation of the Henry’s law constant at temperatures from 0°C to at least 100°C and at pressures from saturation to at least 10 bar. This substantially enhances accuracy of calculations based on the Henry’s law constant such as environmental partitioning or various processes in remediation technologies. A newly established database of critically reviewed and thermodynamically consistent properties of hydration for selected organic solutes at reference conditions was employed as the key part of the training sets in evaluation of bond contributions for the properties of interest. Some details regarding this database will be also covered in the paper.
Understanding PCBM’s Unique Structural and Dynamical Properties through Computation and Experiment

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Phenyl-C61-butyric acid methyl ester (PCBM) is a fullerene-based material of great technological interest, due to its use as an electron-acceptor material in organic solar photo-voltaic cells (OPVCs). State of the art studies report that for devices with a thickness of 200 nm, PCBM and poly(3-hexylthiophene-2-5-diyl) blends can achieve solar-energy harvesting efficiencies of up to 10%\cite{1}. One of the key factors for PCBM’s success in such devices is its ability to optimise its structure and morphology through solvent and thermal annealing. This is something which has also been predicted from theory. Classical molecular dynamics studies have shown that the resultant structure of solid and amorphous PCBM differs drastically dependent on the thermal history and the temperature at which solvent extraction is performed\cite{2}. Furthermore PCBM features a very rich behaviour regarding its thermophysical properties, notably the thermal conductivity of thin films is the lowest measured in materials with energy applications\cite{3}.

In order to devise a strategy to increase harvesting efficiencies, it is crucial that we gain insight into the structural and dynamical properties of PCBM. Fullerene based materials have previously been shown to have a very rich set of dynamical behaviours. In particular, fullerene itself was shown to undergo an order-disorder transition in the form of a rotor phase above 90 K\cite{4}. We present quasi-elastic neutron scattering experiments that provide insight on such a transition in PCBM, as well as elucidating the collective mechanisms responsible for its ultra low thermal conductivity. Furthermore we perform classical and ab initio molecular dynamic simulations to gain microscopic insight into these phenomena and discuss the overall impact that this may have for the future manufacture of OPVCs.
Thermal coupling effects were first experimentally observed in the late 19th century by Ludwig and Soret, who famously saw the separation of binary fluids as a response to an applied temperature gradient (The Soret effect). Later experiments have exposed the complexity of the Ludwig-Soret effect. In particular it has been found that the Soret coefficient of binary mixtures can feature sign inversion. A widely studied example is represented by aqueous solutions which feature an “inversion temperature”. Above this temperature the salt is thermophobic (ions migrate towards the cold region), however below they become thermophilic [1]. This general phenomenon is also observed in biomolecules [2]. A full microscopic explanation of this phenomenon is still missing, although some advances have been reported recently [3].

We have recently shown via simulation and Non-Equilibrium Thermodynamics that the permanent dipole moment of water adopts a preferred orientation by coupling to a temperature gradient, which as a result can give rise to electric fields of the order of $10^6$ V/m for an applied temperature gradient of $10^3 \, \text{K}/\mu\text{m}$ [4].

In this contribution we report the existence of an inversion temperature for the thermal polarisation of water, where the polarisation field reverses its sign. For the widely used SPC/E model we find an inversion temperature $\sim 300$ K at pressure $\sim 400$ bar. This is to best of our knowledge the first example of a temperature inversion in the thermal-polarisation of a pure liquid. Through the theory of non-equilibrium thermodynamics we provide microscopic insight into the reversal of this collective property and discuss the possibility of similar such inversion in other single component fluids.
Supercooled water exhibits spectacular anomalies which have been a subject of debates for decades. Twenty years ago Poole et al. suggested that the anomalous properties of supercooled water may be caused by a critical point that terminates a line of liquid-liquid separation of lower-density and higher-density water, hidden below the line of homogeneous ice nucleation. This phenomenon can be viewed as “water’s polyamorphism”. Recent accurate simulations of the ST2 model of water favor the existence of this metastable transition. A phenomenological model, in which liquid water at low temperatures is considered as “solution” of two hydrogen-bond network structures with different entropies and densities explains why supercooled water may unmix and nicely describes the thermodynamic anomalies in supercooled water and in some popular water-like models, such as mW and ST2. The existence of two alternative structures in water may (ST2) or may not (mW) result in liquid-liquid separation, depending on the nonideality of mixing of these two alternative structures. The two-state thermodynamics has been recently generalized to aqueous solutions for describing the liquid-liquid transitions stemming from the hidden liquid-liquid transition in pure water.

In supercooled water, anomalies in dynamics closely follow the thermodynamics anomalies. However, contrarily the vapor-liquid transitions, the dynamic anomalies in supercooled water have been attributed to a structural and viscoelastic relaxation. While the dispersion of sound near the vapor-liquid critical point is solely an effect of the diffusive relaxation of critical density fluctuations, the dispersion of sound in supercooled water is a viscoelastic relaxation phenomenon. Moreover, supercooled water fundamentally differs from water in the vapor-liquid critical region due to a non-conserved nature of the order parameter associated with the orientation of hydrogen bonds in water. Phenomenologically, this order parameter can be viewed as the extent of “reaction” between two alternative structures of water. Rather than obeying the diffusive space-dependent decay, the relaxation of the non-conserved order parameter is independent of the wave number. This would have far-reaching implications for various dynamic properties of supercooled water.
A popular hypothesis that explains the anomalies of supercooled water is the existence of a metastable liquid–liquid transition hidden below the line of homogeneous nucleation. If this transition exists and if it is terminated by a critical point, the addition of a solute should generate a line of liquid–liquid critical points emanating from the critical point of pure metastable water. We have analyzed thermodynamic consequences of this scenario. In particular, we consider the behavior of aqueous solutions of sodium chloride. We find the behavior of the heat capacity in supercooled aqueous solutions of NaCl, as reported by Archer and Carter to be consistent with the presence of the metastable liquid–liquid transition. The anomalous behavior of the isobaric heat capacity at constant salt concentration is controlled by the Krichevskii parameter, which reflects the shape of the critical line in solution. We have also compared the predictions of our thermodynamic analysis with the results of simulations of the TIP4P model. We elucidate the nonconserved nature of the order parameter (extent of “reaction” between two alternative structures of water) and the consequences of its coupling with conserved properties (density and concentration).
The opposite sides of the liquid-liquid coexistence curve describing a mixture of isobutyric acid (IBA) + water converge to an upper consolute point at an acid concentration of 4.4 M and a temperature near 26 C. Isobutyric acid is a weak acid, which ionizes in water to form hydronium ion and isobutyrate ion. When a sample of IBA + water at a temperature above 26 C comes into equilibrium with an ion exchange resin in the hydroxide form, isobutyrate ion exchanges with the hydroxide ion. The amount of acid exchanged is proportional to the difference between the initial acid concentration and the concentration remaining after equilibrium. We have determined the amount of acid adsorbed as a function of the initial acid concentration for isotherms at 27, 29, 31, and 38 degrees. The data collected along the 38 C isotherm lie on a straight line when plotted according to the Langmuir adsorption equation. By contrast, each of the Langmuir plots associated with the isotherms at 27, 29, 31 degrees, respectively, exhibits a maximum at an equilibrium acid concentration near 4.4 M. These maxima indicate that isobutyrate ion is increasingly rejected by the resin as the critical point is approached. At 27 C, which is the isotherm closest to critical, the uptake of isobutyrate ion is smaller by a factor of 100 than would be expected on the basis of a straight line Langmuir plot. Using Donnan ion exchange theory, we derive an equation linking the swelling pressure in the resin to the osmotic pressure in the exterior liquid phase. We find that the maximum exhibited by the Langmuir plots has its origin in the divergence in the osmotic compressibility as the critical point is approached. The latter is a common feature of the consolute point of a binary liquid mixture.
Impact of Organic Solvents on the Diffusivity of Carbon Dioxide in Alkanolamines

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Optimal selection of solvents and process designs for the purification of industrial gas streams requires a fundamental understanding of the rate of mass transfer of acid gases from the gas phase into the liquid phase. Commonly, the gas industry uses aqueous alkanolamine solvents for the removal of acid gases and blended systems with organic solvents to selectively target additional contaminants such as organic sulfur compounds. The mass transfer of acid gases to aqueous alkanolamine solvents is a complex process that can be significantly impacted by the addition of an organic solvent. Understanding the effect of organic solvent addition on key thermophysical properties such as the liquid phase diffusivity is critical for accurate process design. However, direct experimental measurement of these properties is challenging or impossible due to the presence of chemical reactions, and complicated experimental setups. Analogies to similar compounds are typically required in order to make use of experimental data. Molecular simulation thus offers an attractive alternative to probe these systems. In this paper, we use molecular dynamics simulations to understand the effect of blending aqueous alkanolamines with organic solvents on the diffusion of carbon dioxide. Systematic studies are presented comparing the diffusivity of carbon dioxide in aqueous alkanolamines and blends with methanol and triethylene glycol. Conclusions relevant to gas treating applications are drawn from these studies.
Towards TOTM as an Industrial Reference Fluid for Viscosity at High Temperatures and High Pressures

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Tris(2-ethylhexyl) trimellitate (TOTM) was recently suggested as an industrial reference fluid for high viscosity at elevated temperature and pressure. Viscosity [1] and density [2] data have been published covering the temperature range (303 to 373) K and at pressures up to about 65 MPa. The viscosity covered a range from about (9 to 460) mPa.s. In the present communication we examine several other aspects of the choice of TOTM that must be satisfied if it were to be adopted as an industrial standard. First, we present values for the viscosity obtained with a different sample of TOTM, for comparison with the previous data, to examine consistency among different samples. Furthermore, we report a study of the effect of water contamination on the viscosity of TOTM. Finally, in order to support the use of TOTM as a reference liquid for the calibration of capillary viscometers, values of its surface tension, obtained by the pendant drop method are also provided.

References

A Rigorous Methodology for Development and Uncertainty Analysis of Group Contribution Based Property Models

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Property prediction models are a fundamental tool of process modeling and analysis, especially at the early stage of process development. Furthermore, property prediction models are the fundamental tool for Computer-aided molecular design used for the development of new refrigerants. Group contribution (GC) based prediction methods use structurally dependent parameters in order to determine the property of pure components. The aim of the GC parameter estimation is to find the best possible set of model parameters that fits the experimental data. In that sense, there is often a lack of attention on numerical and statistical challenges associated with model development and analysis. These challenges include for example (i) performance of optimization algorithms used for finding minimum of the objective function for the parameter estimation, (ii) assessment of parameter estimation errors, (iii) assessment of property model prediction errors, (iv) effect of outliers and data pre-treatment, (iv) formulation of parameter estimation problem (e.g. weighted least squares, ordinary least squares, robust regression, etc.) In this study a comprehensive methodology is developed to perform a rigorous and step-by-step assessment and solution of the pitfalls involved in developing models.

The methodology takes into account of the following steps.

1) Experimental data collection and providing structural information of molecules.

2) Choice of the regression model: a) ordinary least square b) robust or c) weighted-least-square regression.

3) Initialization of estimation by use of linear algebra providing a first guess.

4) Sequential parameter and simultaneous GC parameter by using of 4 different minimization algorithms.

5) Thorough uncertainty analysis: a) based on asymptotic approximation of parameter covariance matrix b) based on boot strap method. Providing 95%-confidence intervals of parameters and predicted property.

6) Performance statistics analysis and model application.

The application of the methodology is shown for a new GC model built to predict lower flammability limit (LFL) for refrigerants. The GC model uses the Marrero-Gani (MR) method which considers the group contribution in different levels both functional and structural. The methodology helps improve accuracy and reliability of property modeling and provides a rigorous model quality check and assurance. This is expected to further their credibility and robustness in wider industrial and scientific applications.
The description of wetting behavior in terms of state variables (i.e. temperature, pressure, composition) and conformational parameters (i.e. chain lengths, interaction solvent-solute, etc) becomes relevant in various technological applications. Particularly, the variation of these properties with process conditions is one of the main factors governing the design and operation of the equipment involved in physico-chemical processes and in chemical transformations. In the present work we report predictions of sub-critical vapor-liquid-liquid equilibrium (VLLE) and interfacial properties for binary composed by tangent spherical segments of equal size. Two complementary methods, namely Molecular Dynamics simulations (MD) and Density Gradient Theory (DGT) have been used for describing the interfacial region, thus allowing predicting both the macroscopic and molecular details of mixtures exhibiting wetting behavior. DGT calculations rely on the prediction of the VLLE by means of the soft-SAFT equation of state (soft SAFT-EoS). Preliminary results show that a wetting transition along the three-phase line (from partial a total wettability) is obtained when the chain length increases, from a monomer + monomer case of type-V Lennard-Jones.
Performance Checks and Validation of High Temperature Guarded Hot Plates

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The guarded hot plate method (GHP) is the reference technique for measuring thermal conductivity of insulation materials and medium conductive materials. The requirements for the design and for checking performance of guarded hot plate apparatus used around room temperature are well documented in standards such as ISO 8302, ASTM C177, EN 12664 and EN 12667. Complying with the requirements of those standards allow to perform thermal conductivity measurements with relative uncertainty better than 5% and to get reproducibility better than 1%. For guarded hot plates used above 100°C, it is almost impossible to fully comply with standards specifying low temperature guarded hot plates because of technical constraints. A group of five National Metrology Institutes (NPL, CMI, LNE, MKEH, PTB) in EU are collaborating in a three-year project for improvement of measurements of thermal conductivity of insulation materials and thermal protection materials up to 800°C. Those institutes have developed or are developing GHPs for temperatures from 100 to 800°C. Those instruments will be commissioned as national references if they reach the objective of relative uncertainty better than 5%. For validating high temperature GHPs and assessing uncertainties, particular techniques and procedures must be used. Validations aims to show mainly that the heat flow is unidirectional in the metering area and that parameters used for the calculation of thermal conductivity are known with the appropriate uncertainties. Global validations are also performed to show that results remains coherent for different conditions of measurement. The techniques of validation, specific to the configuration of each apparatus are described in detail and examples of numerical results are given.
Acknowledgements

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Novel Peltier-Element-Based Adiabatic Scanning Calorimeter for the Measurement of Phase Transitions in Condensed Matter Systems

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Adiabatic scanning calorimetry (ASC) (introduced in the early 1980s) has received only limited attention because of the complexity in operating the old types of ASC set-ups [1]. Here we present a novel Peltier-element-based adiabatic scanning calorimeter (pASC), that eliminates this and also several issues of differential scanning calorimetry (DSC), while achieving accuracy close to that of adiabatic heat-step calorimeters and very high resolution in temperature[2]. The working concepts of ASC and DSC are based on the same expression for the heat capacity $C=P/\left(dT/dt\right)$, with $P$ the applied or measured power and $\left(dT/dt\right)$ the measured or applied temperature rate. The essential difference between ASC and DSC lies in the implementation of this expression. In an ASC, one applies constant power to the sample and derives the changing rate from the recorded temperature evolution $T(t)$ with time $t$. In a DSC, a constant rate is imposed and the changing power to comply with the constant rate requirement is measured: thus exactly the opposite. Moreover, the constant power in ASC simultaneously results in the temperature dependence of the enthalpy $H(T)=Pt$, including the latent heat when present. Investigations of some melting points will show that while ASC results in thermodynamic equilibrium data, DSC results are essentially rate dependent [3,4]. It will also be shown that pASC not only can run in the default constant power mode, but also in the classical heat-step or in DSC-type modes.

References
Characterization of Thermal Transport in One-Dimensional Microstructures using Johnson Noise Electro-Thermal Technique

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This work reports on the development of a Johnson noise Electro-thermal (JET) technique to directly characterize the thermal conductivity of one-dimensional micro/nanoscale materials. In this technique, the to-be-measured micro/nanoscale sample is connected between two electrodes, and is subjected to steady-state Joule heating. The average temperature rise of the sample is evaluated by simultaneously measuring the Johnson noise over it and its electrical resistance. The system’s Johnson noise measurement accuracy is evaluated by measuring the Boltzmann constant ($k_B$). Our measured $k_B$ value ($1.375 \times 10^{-23}$ J/K) agrees very well with the reference value of $1.381 \times 10^{-23}$ J/K. The temperature measurement accuracy based on Johnson noise is studied against the resistance temperature detector method, and sound agreement (4%) is obtained. The thermal conductivity of a glass fiber with a diameter of 8.82 μm is measured using the JET technique. The measured value: 1.20 W/m·K agrees well with the result using a standard technique in our lab. The JET technique provides a very compelling way to characterize the thermophysical properties of micro/nanoscale materials without calibrating the sample’s resistance-temperature coefficient, thereby eliminating the effect of resistance drift/change during measurement and calibration. Since JET technique does not require resistance-temperature correlation, it is also applicable to semi-conductive materials which usually have a non-linear I-V relation.
Liquefied Natural Gas (LNG) is a significant contributor towards meeting the continuously mounting global demand for energy. According to Exxon Mobil Corporation [1], the global demand for LNG is projected to rise by 65% within the next three decades despite the slow demand growth within the last year [2]. This demand is primarily due to the expansion of China, who has become extremely influential in world energy markets due to their ongoing expansion and subsequent increasing energy demand [3]. Consequently, flow assurance within LNG processing facilities has become a major technical and economic issue. The avoidance or remediation of the formation and subsequent deposition of long-chain hydrocarbon (C6+) solids is one key aspect of flow assurance. Under the cryogenic temperatures and high pressures at which LNG processing facilities operate, these hydrocarbons can precipitate out of the LNG and accumulate in the process equipment causing blockages. The ability to predict solids deposition rates depends on many factors, one of which is currently being examined in this work: the thermodynamic equilibrium between LNG and hydrocarbon solids. A commercial differential scanning calorimeter (DSC) was used to determine the melting temperatures for hydrocarbon mixtures containing components analogous to those that precipitate in LNG processing. This apparatus is capable of attaining temperatures as low as 77 K and pressures up to 6 MPa thereby simulating the industrial operating conditions at which precipitation occurs. Melting temperature measurements of LNG analogues under both ambient and plant operating conditions will be presented, together with an analysis of the impact of both solute and solvent composition.

References

The objective of thermodynamic consistency tests is to show the likely absence of systematic errors. The practical uses are (i) to referee between different data sets on the same system, (ii) to justify confidence in the chemical process equipment designed from the data, and (iii) to ensure data of the highest quality for experimental standards and for testing and extension of theory. Binary PTxy (pressure-temperature-liquid mole fraction-vapor mole fraction) vapor-liquid equilibrium (VLE) data are redundant according to the phase rule. Hence, differential and integral thermodynamic consistency tests can be constructed from the Gibbs-Duhem equation. In contrast, Px or Tx (PTx) data are the minimum necessary to specify VLE so that the Gibbs-Duhem tests are not possible. However, $G^f$ data derived from PTx data measured at several temperatures can be compared to calorimetric $H^f$ data with the Gibbs-Helmholtz equation,

$$-RT\left[\frac{\partial (G^f/RT)}{\partial T}\right]_{P,x} = H^f$$

This comparison can be used as a thermodynamic consistency test for PTx data.

Results are presented for Gibbs-Helmholtz analysis of ebulliometrically-determined PTx data for the systems water + acrylic acid, 1, 2-propylene glycol + ethylene glycol, 1, 3-propylene glycol + ethylene glycol, and water + N-methylethlenediamine. The system ethanol + water is revisited to demonstrate the effects on Gibbs-Helmholtz analysis from using a local-composition model with fixed temperature dependence instead of using a Redlich-Kister expansion at each temperature. In addition, the special Gibbs-Helmholtz problems presented by nearly-ideal systems are analyzed.
Non-Equilibrium Concentration Fluctuations Induced by the Soret Effect in Microgravity

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Non-Equilibrium fluctuations are spatially long-ranged. Hence, even in macroscopic systems the spontaneous thermodynamic fluctuations "feel" the boundaries and, in general, both their intensity and their dynamics depend on the boundary conditions. Here, a layer of a binary liquid mixture that is bounded by two plates maintained at two different temperatures is considered. The Soret effect induces a stationary concentration profile, and fluctuating hydrodynamics (FHD) provides a theoretical framework to study spontaneous concentration fluctuations around it. In this problem, realistic boundary conditions are no diffusion flow at the two bounding plates for the concentration fluctuations and no-slip for the velocity fluctuations. In the absence of gravity (or in microgravity) and for incompressible flow in a large-Lewis-number approximation, the FHD equations can be exactly solved, and a relatively simple analytical expression can be obtained for the time-correlation-function of the concentration fluctuations accounting for realistic boundary conditions. It turns out that, in this particular case of no gravity, the dynamics of the fluctuations is not affected by the gradient and is the same as if the system were at equilibrium at an average concentration. However, the intensity of the fluctuations is strongly affected by the presence of the gradient. The present solution for realistic boundary conditions will be compared with previous analytical results for unrealistic boundary conditions (free-slip and stationary concentration boundaries). Similarly, the current theoretical results will also be compared with available experimental information.
The accurate nondestructive and real time determination of the critical dimensions of oxide nano-films on periodic nano-structures has potential applications in nanofabrication techniques. Mueller ellipsometry is fast, accurate, nondestructive, and can be used in air. This study used the elements of a Mueller matrix of specular reflection, which is based on a Mueller ellipsometry method, to evaluate the thickness of an oxide nano-film on an aluminum grating surface. By using the rigorous coupled-wave analysis (RCWA), we decomposed the Mueller matrix to obtain the relationship between the evaluated polarization properties of reflected light and the dimensions of oxide nano-films on aluminum grating surfaces. We also quantitatively analysed the Mueller matrix elements variation by the thicknesses of top, sidewall, and bottom oxides, considering the nonuniform naturally oxide nano-films on grating structures. The results show that the elements of Mueller matrix shift with the increasing of the uniform thickness of oxide at a fixed wavelength. Moreover, as oxide nano-films on grating structures are nonuniform, the impact of the thickness of side wall oxide on the Mueller matrix elements is more obvious than that of top and bottom oxides at the relative larger incidence wavelength range. The finding of this work may facilitate the nondestructive and real time measurement of the thickness of oxide nano-films on metal grating structures in which the metal is easily oxidized.
Fusion enthalpy is an important physical property of the phase change materials (PCM). The magnitude of the fusion enthalpy and melting point influences the actual performance of PCM. Salts have been most preferable high-temperature PCM and they have been widely used for thermal energy storage in the nuclear fuel molten salt reactors or thermal insulation materials in space flight because of their high fusion enthalpy per unit mass. Reliable data of fusion enthalpy are necessary for the process design. However, because of the difficulties in the high temperature of measurement, some of the fusion enthalpy data of salts were derived from phase diagrams or were averaged of widely scattered values. An empirical relationship can be used to estimate fusion enthalpy and a numerical value can be provided when there are no experimental data. Estimations are also useful in selecting the most probable experimental value in cases where two or more values are in significant disagreement. The purpose of this paper is to estimate the fusion entropy of salts based on a uniform model. Fusion enthalpies are calculated from fusion entropies and experimental melting temperature of the solid based on Walden’s rule. The physical meaning of total entropy of melting is the sum of all the entropies of transition and the entropy of melting from the crystal to the isotropic liquid. According to Bondi (1968), the total entropy of melting is the sum of its positional, rotational, and conformational contributions. Based on Walden’s rule, the entropy of melting for some compounds with little flexibility equals to a constant. Dannenfelser et al. (1993) found that the total entropy of melting for rigid compounds can be predicted by extending Walden’s rule to include the effect of molecular rotational symmetry. They related the rotational entropy of melting to the external rotational symmetry number of the molecule. Following equation can be obtained by combining these concepts. In this paper the calculation of entropy of melting is extended further and refined so that it is applicable to chloride and fluoride salts. The molecular symmetry number is refined, and the molecular flexibility is correlated with an empirical relationship. The equation can be used to predict both 1-1 and 1-2 type inorganic salts. Special satisfactory results were obtained for fluoride salts.
Thermophysical Properties of 1-Methyl-3-Octylimidazolium Tetrafluoroborate at High Pressures and Over Wide Range of Temperatures

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Room temperature ionic liquids (ILs) are salts that are liquids at ambient temperatures and pressures. They are excellent solvents for a broad range of polar organic compounds and they show partial miscibility with aromatic hydrocarbons. IL’s are composed of bulky ions, have very small vapor pressure, low melting point, high solvating capacity, high ionic conductivity and high thermal stability, which make them attractive for practical applications. Thermophysical properties of IL’s make them very suitable as heat transfer fluids and short heat term storage in power plants. Therefore, the thermodynamic and structural properties of ILs are urgently needed for the design of many technological processes. In this presentation, we inform about the \((p, \rho, T)\) data of 1-methyl-3-octylimidazolium tetrafluoroborate \([\text{OMIM}][\text{BF}_4]\) at \(T = (283.15 \text{ to } 413.15) \text{ K}\) and pressures up to \(p = 140 \text{ MPa}\) with an estimated experimental relative combined standard uncertainty of \(\Delta \rho / \rho = \pm (0.01 \text{ to } 0.08) \%\) in density. The measurements were carried out with an Anton- Paar DMA HPM vibration- tube densimeter. The temperature within the measuring cell where the U – tube is located is controlled using a thermostat (F32 - ME Julabo, Germany) with an error of \(\pm 10 \text{ mK}\) and is measured using the (ITS-90) Pt100 thermometer (Type 2141) with an experimental error of \(\pm 15 \text{ mK}\). Pressure is measured by pressure transmitters P-10 and HP-1 (WIKA Alexander Wiegand GmbH & Co., Germany) with a relative uncertainty of (0.1 and 0.5) \% respectively, of the measured value. An empiric equation of state fitted to the experimental \((p, \rho, T)\) data of \([\text{OMIM}][\text{BF}_4]\) as a function of pressure and temperature is presented. This equation is used for the calculation of thermophysical properties of this IL, such as isothermal compressibility, isobaric thermal expansibility, thermal pressure coefficient, internal pressure, isobaric and isochoric heat capacities, speed of sound and isentropic expansibility. The literature \((p, \rho, T)\) values of \([\text{OMIM}][\text{BF}_4]\) were compared with our values and good agreement was obtained.
The Gibbs entropy postulate is a cornerstone of mesoscopic non-equilibrium thermodynamics. I will discuss its general applicability to a wide diversity of systems that depart from the traditional local equilibrium assumption. The applicability extends from physical processes, such as inertial effects in diffusion, to biomedicine, including the characterization of leukemia on multidimensional morphological and molecular landscapes.

References

Molecular dynamic methods applied to spherical molecules interacting with hard cores and suitably adjusted soft repulsive shoulders next to attractive square wells have given results that are in reasonably good agreement with measurements on several single component fluids both far from gas-liquid critical points and reasonably close to their critical points. But when quite close to a critical point, highly accurate results require larger and larger numbers of particles in the calculations, owing to the important role played then by density fluctuations of increasingly long wavelengths. Because calculations with very large numbers of particles can become prohibitively expensive and time consuming, it may be of interest to see whether "global" renormalization-group additions to easily achievable molecular dynamics results for fewer particles can result in substantial improvements in predicting behavior in the near vicinity of critical points. Some results, using essentially the method described in J. A. White, J. Chem. Phys. 112 (2000) 3236, will be reported for near critical point behavior in the vicinity of the gas-liquid critical point for water, and to explore what might be expected near its possible second, low-density high-density liquid-liquid critical point below the normal freezing point.
Determination of Interfacial Properties using a PC-SAFT Based Classical Density Functional Theory for Fluid Mixtures of Industrial Interest

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A recent development of a PC-SAFT based classical density functional theory (DFT) is applied to the determination of interfacial properties of pure fluids and mixtures of industrial interest. Initially, the DFT formalism is described and the methodology for the property calculations explained. The consistency of this approach allows the determination of interfacial properties for fluids using the PC-SAFT equation of state parameters determined from bulk physical property data, such as vapor-liquid-equilibrium and densities. This methodology is an excellent alternative for the predictions of interfacial property of fluids and extrapolation to high pressure ranges where experimental measurements becomes challenging.
With its extraordinary optical properties and thermal conductivity, the two-dimensional carbon allotrope graphene has demonstrated as an excellent candidate in solar cells, microelectronics, optoelectronics, etc. Recently, graphene has been massively produced and deposited on various substrates by the Chemical Vapor Deposition (CVD) method. Yet the different choices of substrate greatly influence the optical properties of deposited graphene. Thus, to broaden and deepen its wide application in the scientific community, it’s crucial to understand and predict the interface effect on the thermophysical parameter dielectric function of graphene deposited on different substrates. In this work, the dielectric functions of graphene deposited on metal copper and quartz crystal are wholly investigated by the ellipsometry experiments and first-principles calculations. The state-of-the-art infrared-variable angle spectroscopic ellipsometry (IR-VASE) and visible-variable angle spectroscopic ellipsometry (V-VASE) are applied to experimentally measure the room-temperature dielectric functions of graphene spanning from the spectral range 0.19-33 μm. By comparing the measured dielectric functions of graphene deposited on the two different substrates with that of isolated graphene from previous literatures, the interface effect is analyzed and discussed. On the other hand, to intrinsically understand and predict the interface effect, the first-principles methods are applied to calculate the electronic band structure and dielectric functions of isolated graphene and those deposited on metal copper and quartz crystal. The calculated dielectric functions of isolated graphene are compared with experimental measurements to verify the first-principles calculations. The electronic band structure and density of states of isolated and deposited graphene are investigated to intrinsically analyze and understand the interface effect. In sum, this works aims to provide some insight into understanding and predicting the dielectric functions of graphene deposited on different substrates.
Measurements and Calculation of CO$_2$-Reservoir Oil Minimum Miscibility Pressure using a Novel Rising Bubble Apparatus

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CO$_2$-oil Minimum Miscibility Pressure (MMP) is the key parameter for the design and operations of successful CO$_2$ miscible flood project. The study objective is to develop mathematical models of predicting pure CO$_2$-oil MMP. Part-1 of the study consisted of the experimental work based on the Rising Bubble Apparatus to measure CO$_2$-oil MMP for different Omani light oil reservoirs and part-2, contained the development of mathematical models by using the Artificial intelligence techniques based on the resulting MMP values obtained from the experimental work in Part-1 and the literature MMP data. The Artificial intelligence techniques utilized the Artificial Neural Network (ANN) and the Particle Swarm Optimization (PSO) methods. The resulting percent deviations of 4.69 and 4.33 were achieved by using the developed ANN and PSO models for the Omani oil samples MMP data respectively. Thus, the developed ANN and PSO models resulted in more accurate predictions of CO$_2$-oil MMP than the literature models. The ANN and PSO models were constructed based on the approach that the literature CO$_2$-oil MMP data were used for the training process of the models and the experimental CO$_2$-oil MMP results for the Omani oil samples were utilized for the testing of models. This gives an advantage to the developed ANN and PSO models that they are capable of being applied for Oman light oil reservoirs and more widely. The developed mathematical models provide an accurate and fast method for the prediction of CO$_2$-oil MMP.
Dynamic Heterogeneity of Ionic and Non-Ionic Drugs Studied Near the Glass Transition by Calorimetric, Dielectric and Mechanical Techniques

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Molecular dynamics of the deeply supercooled liquids is highly heterogeneous. It means that molecules only a few nanometers away from each other may have relaxation rates that differ by several orders of magnitude. Near the glass transition, a significant increase in the length scale of molecular dynamics is observed, which suggests that the spatial heterogeneities can be responsible for the glass transition dynamics [1]. Therefore, in the last half-century, the dynamic heterogeneity of various glass-former liquids has been intensively studied to gain a better insight into our understanding of the glass transition and the related phenomena. The latest theoretical, simulation and experimental investigations suggest that there is a relationship between the glass formation, dynamic heterogeneity, and crystal nucleation, which can play an important role in recrystallization mechanism of amorphous materials [2,3]. One of the most important questions which arises in the heterogeneous picture of molecular dynamics is “how the different molecular interactions affect the degree of the dynamic heterogeneity?”. Based on calorimetric, dielectric and mechanical measurements, we evaluate the length scale of heterogeneity for several drugs which are bases (i.e. non-ionic liquids) as well as their hydrochloride salts that belong to protic ionic liquids. Such studies are very interesting, because molecules of these pharmaceuticals have nearly the same chemical structure but their intermolecular interactions are completely different. In this way, we check how the different kinds of intermolecular interactions influence the dynamic heterogeneity of molecular dynamics near the glass transition.

References

Often, a calibrated pressure vessel is used as a gas source and/or a gas collector to calibrate gas-flow meters. With flow calibrations in mind, we established the feasibility of determining the mass of the argon contained within a 0.3 m³, commercially-manufactured, pressure vessel (a “tank”) with an uncertainty of 0.14 % by combining measurements of the argon pressure, the frequencies of microwave and acoustic resonances within the pressure vessel, and an equation of state for argon. Previously published microwave measurements determined the tank’s internal volume \( V_{\text{micro}} \) with a standard uncertainty of 0.06 % and they also determined the thermal and pressure expansion of the volume. [M. R. Moldover et al., *Meas. Sci. Tech.* (in press).] The microwave results accurately predict the lower acoustic resonance frequencies \( f_{\text{calc}} \). In the zero-pressure limit, the average deviation \( \langle f_{\text{meas}}/f_{\text{calc}} - 1 \rangle \) = 0.00025 ± 0.00051 based on the five lowest-frequency acoustic modes. At 0.6 MPa, \( \langle f_{\text{meas}}/f_{\text{calc}} - 1 \rangle \approx -0.00071 \pm 0.00082 \) for the lowest three modes, after correcting \( f_{\text{meas}} \) for the tank’s calculated pressure-dependent center of mass motion. The relative uncertainty of the argon density is twice the uncertainty of \( f_{\text{meas}}/f_{\text{calc}} \); therefore, these three modes determine the mass of the argon in the tank at 0.6 MPa with an estimated error of 0.16 %. The values \( f_{\text{meas}} \) determine the average speed of sound (and therefore the average temperature) of the argon in the tank. First order perturbation theory predicts that the values of \( f_{\text{calc}} \) are insensitive to uniform temperature gradients. We confirmed this insensitivity by imposing a temperature gradient (in one case, 13 K top to bottom) on the tank. We conclude that resonance techniques can be used to weigh compressed gas in much larger tanks and at higher pressures in un-thermostatted environments; therefore, these techniques will have many applications in gas metrology.
Molecular Simulation of Carbon Dioxide, Water and Kaolinite Interactions

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Safe long-term storage of carbon dioxide (CO₂) will reduce CO₂-emissions to the atmosphere. This can be achieved by injecting captured CO₂ in geological formations. CO₂ injection in reservoirs is also a well-known method used in enhanced oil-recovery (EOR). Lastly, injection of carbon dioxide in methane hydrate is a promising method, both due to energy aspects as well as climate aspects. The above mentioned reasons have several challenging common problems, there among, how the microscopic interactions between reservoirs species governs the behavior of injected CO₂. To study the behavior of super-critical CO₂ at the nanoscale, we have performed Molecular Dynamics (MD) simulations of a water, CO₂ and clay system. The mineral used in our simulations is kaolinite, a common clay found in the earth’s crust. We have initially focused on a slab of kaolinite with the hydrophilic gibbsite layer exposed to a water phase that is in contact with a super-critical CO₂ phase. The interactions of the CO₂ phase with the water phase have been analyzed. As well as the impact of varying temperature on CO₂ dissolution from the super-critical phase into the kaolinite adsorbed water. Results shows that water adsorbs strongly on the gibbsite surface of kaolinite, but this strongly adsorbed water also creates following exclusion zones where adsorption of CO₂ can be facilitated.
To slow down global warming there is an increasing focus on reducing carbon dioxide (CO$_2$) emissions to the atmosphere. Geologic storage of CO$_2$ is one method that can contribute to nations reaching the desired limits on emissions of greenhouse gases. Long-term storage of CO$_2$ in geological formations requires knowledge on several different trapping processes that run on different time-scales. In order to understand these complex systems on a field-scale, it is important to understand the nanoscale behavior. Among other, how the solubility trapping of CO$_2$ occurs. Dissolved CO$_2$ can react with reservoir rocks and form carbonate minerals. This process is known as mineral trapping and is the most stable form of storage. But insight into the microscopic effects that governs the macroscopic thermodynamic observables can often be hard to obtain, especially when it comes to interfacial systems. We have used molecular dynamics (MD) and focused on carbon dioxide and water adsorbed on calcite. The system consisted of a calcite slab with the (1014) surface exposed to a water phase interacting with a super-critical CO$_2$ phase. The effect of varying temperature was also investigated through several large-scale simulations at different temperatures. Results show that the density of water increases towards the mineral surface. This creates voids that can facilitate increasing dissolution of CO$_2$ into the water phase.
Absorption material to ionizing radiation results in absorption of energy by matter in the form of heat energy and a corresponding increase in temperature. Absorption of radiation matter is accompanied not only by ionization of air in the reference chamber in a Geiger counter inside the dosimeter, but also an increase in temperature of the material. Hence, by measuring the temperature rise can be determined dose of radiation. This method can be used to determine the energy yield of burned in nuclear reactors on fast neutrons of radioactive waste. On the other, the thermodynamically equilibrium systems in which there are processes of isolation and heat loss (this is not the only nuclear reactors but also any heating system from the boiler to the brick furnaces) accent can be moved to the phenomenon of temperature increase. Thus, we come to the need for a temperature dose. Thermal dose - is an integral characteristic of the temperature influence on the object is equal to the area of the graph of temperature versus time. In the international system of units the temperature dose has dimension degree for a second. At negative temperatures influence is characterized by negative doses. For practice the stand-alone unit named by Stephane (St) – degree for a minute is offered. It is visible that 1 St is equal 60 degree∙sec. To measure the calorific value were made antiradonic ceramic furnaces with effect of low-temperature gasification that has high efficiency, in which 10 liters of boiling water for 5-10 minutes with a mixture of dry rubber and waste wood. The area under the curve on a graph of temperature increase in water volume determines the measured value - the temperature corresponding dose S. balance equation for the water heating process is given by S=kHmt where S-temperature dose, k - coefficient of heat transfer furnace, taking into account the loss of heat from the flue gases, H-calorific fuel (J \ kg), m-fuel weight (kg), t - total time of burning fuel. Found that calorific fuel compositions larch and coal mixture, plastics, rubber, waste oil can vary in the range of 10.2 MJ / Kg to 18.8 MJ / kg. High-energy components such as rubber and plastics proportionally increase power consumption of fuel compositions
What Can We Learn from the Numerical Simulation of Far from Equilibrium Steady States?

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Linear constitutive relations such as Newton's law of viscosity, Fourier's law of heat conduction and Fick's law of diffusion relate thermodynamic forces to fluxes and hence provide the means for closing the partial differential equations describing the conservation of mass, momentum and energy in continuum mechanics. Numerical simulation, using non-equilibrium molecular dynamics (NEMD), provides a powerful means to study the realm of applicability of these constitutive relations, test new relations and formulating new ones. In the last few decades, NEMD has shown that Newton's law of viscosity requires generalizing to account for the non-local dependence of the stress on the strain rate for flowing fluids in highly confined geometries, while Fourier's law of heat conduction must be modified when describing heat flows through the centre of a stationary shockwave, to account for a time lag between the temperature gradient and the heat flux. Central to the success of these numerical discoveries has been the use of well-designed NEMD algorithms able to generate far from equilibrium states with simple boundary conditions. A new simulation algorithm has recently been introduced which enables the generation of Joule-Thomson states of a throttled fluid. The significance of this new method is that it uses simple equilibrium boundary conditions and does not require the use of artificial thermostats. In the main part of this presentation, we describe the algorithm for creating Joule-Thomson states, in both 2 and 3 physical dimensions for fluids using a number of different force laws. We examine the non-equilibrium steady states that are formed, explore the validity of the linear constitutive relations, demonstrate tensor temperature and examine the usefulness of configurational temperature. Simple extensions of the NEMD algorithm include the use of multiple ‘porous plugs’ to generate multiple Joule-Thomson states from a single simulation. These extensions will be discussed together with an analysis of the throttling process in which non-zero flow velocity can be properly accounted for, thus explaining the counterintuitive result of cooling in a gas governed by a purely repulsive force law.
test title

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Tuning interfacial thermal transport is significant for many technologies including nanoelectronics, solid-state lighting, energy generation and nanocomposites, therefore, a better understanding of the atomic-scale structural features contributing to interfacial heat transport between dissimilar materials is needed. Here, we demonstrated an experimental study on the correlation between interfacial thermal conductance and interfacial adhesions across the interfaces of spin coated polystyrene (PS) and sapphire. Time-domain thermoreflectance method (TDTR) is applied to measure the thermal conductance of PS/sapphire interfaces, while their interfacial adhesions are characterized by scratch test experiments. And samples with different kinds of interfaces are manipulated for analyzing the correlation mentioned above. Two major ways are applied to enhance the heat transport across PS and sapphire, including varying rotation speed of the spin-coating process and introducing self-assembled monolayer (SAM) with different terminal groups to tailor polymer and substrate. The results show a great enhancement of the interfacial thermal conductance between PS and sapphire by both ways, which underscore the importance of interfacial bond strength as a bridge to describe and control interfacial thermal transport between polymer and other materials. This fundamental study on the heat transport across ultra-thin polymer and substrate interfaces can impact on the applications of thermal management and the reliability of macro- and micro-electronics, where polymeric and hybrid organic-inorganic thin films have been employed.
The ideal gas heat capacity of potassium atoms is calculated to high temperatures using statistical mechanics. Since there are a large number of atomic energy levels in the Boltzmann sum below the ionization potential, the partition function and heat capacity will become very large as the temperature increases unless the Boltzmann sum is constrained. Two primary categories of arguments are used to do this. First, at high temperatures, the increased size of the atoms is used to constrain the sum (Bethe procedure). Second, an argument based on the existence of interacting ions and electrons at higher temperatures is used to constrain the sum (ionization potential lowering procedure). These two methods are both used, and contrasted, for potassium atoms. When potassium atoms are assumed to constitute a real gas that obeys the virial equation of state, the lowest non-ideal contribution to the heat capacity depends on the second derivative of the second virial coefficient, B(T), which depends on the interaction potential energy curves between two potassium atoms. When two ground state (1S) atoms interact, they can follow either of two potential energy curves. When a 2S atom interacts with an atom in the first excited (1P) state, they can follow any of eight potential energy curves. The values of B(T) for the ten states are determined, then averaged, and used to calculate the non-ideal contribution to the heat capacity.
In this work, we perform molecular dynamics (MD) simulations to study the effects of alkyl chains on the thermal properties of fullerene (C$_{60}$) and fullerene derivatives, and compare the MD prediction with experimental results from Time Domain Thermoreflectance (TDTR). The thermal conductivities of fullerene and its derivative phenyl-C61-butyric acid methyl ester (PCBM) are obtained using non-equilibrium MD simulations for systems with different sizes at room temperature. The results show a length-dependent thermal conductivity for C$_{60}$ but not for PCBM. Around the room temperature, the thermal conductivity of C$_{60}$ obtained from linear extrapolation (up to 33 nm) is 0.2 W m$^{-1}$ K$^{-1}$, while the thermal conductivity of PCBM saturates at ~0.075 W m$^{-1}$ K$^{-1}$ around 20 nm. The different length-dependent behavior of thermal conductivity indicates that the long-wavelength and low-frequency phonons have large contribution to thermal conduction in C$_{60}$, and the decrease in thermal conductivity of fullerene derivatives can be attributed to the strong scattering of those phonons with the alkyl chains. This fact is also indicated by the significant mismatch of vibrational density of states in low frequency regime between buckyballs and alkyl chains in PCBM. The spectra of density of states (DOS) suggest that those dominant phonon modes at ultra-low frequency regime (< 2 meV) are assigned to rotational and vibrational motions of buckyballs in C$_{60}$, which are suppressed by alkyl chains in PCBM.
Comparison of Thermal Diffusivity Apparatus at Very High Temperatures (2500°C)
Demonstrated using Isostatic Graphite

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New metrological facilities for high temperature measurements of thermophysical properties have been developed by European National Metrology Institutes (NMIs), during the joint research project “MetroFission”[1]. These instruments were initially developed to provide reliable measurements up to 2000 °C and to improve the traceability of measurements to the International System of Units (SI). The original validation of these reference facilities, carried out by measuring the thermal properties of an homogeneous material (isostatic graphite), showed that the results obtained were in agreement with literature data. The LNE diffusivimeter has recently been further modified to enable the measurement of thermal diffusivity of solid materials up to 2500 °C, by integrating a new inductive furnace in the existing setup. This paper describes an initial study to compare thermal diffusivity measurements from a commercially based apparatus Netzsch LFA427, with measurements up to 2500°C from the improved NMI diffusivimeter at LNE. The isostatic graphite recommended as a reference material for thermal diffusivity determination, has been characterised on an apparatus based in an industrial setting, normally used for quality control purposes. The extended temperature range of the commercial apparatus (2800°C) made it possible to obtain values for the reference material at higher temperatures than explored within the Metrofission project, and the impact of alternative shielding gases on the resultant thermal diffusivity is described.

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References

Adsorption of Mixtures of Yukawa Fluids on Solid Surfaces

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As precursors to the electric double layers, we examine the adsorption of Yukawa fluids on two types of planar walls: (a) hard walls and (b) Yukawa walls. The first type (hard walls) is for the purpose of establishing the baseline; the second type is to mimic the “electric double layers” of an “electrode/electrolyte” interface, since the Yukawa potential tends to the Coulomb interaction when the decay parameter approaches zero.

Type (I) System:

• Bulk Fluid: (attractive Yukawa interaction)
• Wall: Hard wall.

Type (II) System:

• Bulk Fluid: equal molar mixtures of species A and B molecules. A-A and B-B pairs interact via the repulsive Yukawa potential; A-B pairs via the attractive Yukawa potential.

• Wall: interacting with A molecules via the attractive Yukawa potential; with B molecules via a repulsive Yukawa potential. The wall strength parameter (K) will be varied to simulate charging and discharging conditions.

The Yukawa potential (plus the hard-sphere interaction $u_{HS}$) is defined in terms of an attraction strength parameter $K$, and an exponential decay parameter $Z$. As the decay range parameter $Z$ of the Yukawa potential tends to zero, the Coulomb potential is recovered.

Monte Carlo simulations are carried out at temperatures from $T^* = kT/\varepsilon = 0.76$ to 1.25, and densities $\rho^* = \rho\sigma^3 = 0.4$, 0.7, and 0.8. Type I wall exhibits “depletion” at the two low densities, and “enhancement” at the highest density. Type II walls show more complicated behavior. The quantitative relation is modeled by a newly developed closure-based density functional theory with an OZ3-type bridge function.[1] We delineate the behavior by exhibiting the underlying singlet density, the cavity distribution function, and the chemical potential behavior that give rise to the observed phenomena. Implications on the electric double layers as found on the electrodes in the electrochemistry are explored.

References

Semiclathrate hydrates (SCH) formed with organic salts have empty cages that could encage gas molecules, and some showed high melting temperatures (higher than 300 K) at atmospheric pressure. In this work, phase equilibrium data for the semiclathrate hydrates formed with tetraamylammonium bromide (TAAB: C20H44NBr) + CH4, + CO2, or + N2 were measured in the pressure range of (1.33 to 20.37) MPa and temperature range of (279.8 to 291.9) K at (0.05 and 0.10) mass fraction of TAAB. The experimental data were obtained by employing an isochoric pressure-search method. The results showed that at a given pressure, the temperature required to form double TAAB + CH4, + CO2, or + N2 hydrates was higher than that required for the corresponding pure CH4, CO2 or N2 hydrates. And as the TAAB concentration increased, its effect of enlarging the hydrate stability zone was strengthened. However, the experimental equilibrium temperatures for double semiclathrate hydrates were lower than those for TAAB hydrates formed without guest gases. In addition, the data for double semiclathrate hydrates formed from TAAB generated in this work were compared with those formed from some other semiclathrate hydrate formers (such as tetrabutylammonium bromide, tetrabutylammonium chloride, and tetrabutylammonium fluoride) reported in literature. The comparison demonstrated that at a same mass fraction, the stabilization effect of TAAB was weaker than those of TBAB, TBAC, and TBAF.
We discuss the problem of constructing the equation of state (EOS) for polymeric phase of solid nitrogen at extremely high pressures and temperatures. Helmholtz free energy is represented as a sum of the quasi-harmonic contribution described by the modified Mie-Grüneisen model and anharmonic corrections. EOS describes the behavior of the internal energy, thermal expansion, isothermal compressibility, heat capacity, speed of sound, as well as such specific features of polymeric nitrogen as negative thermal expansion and significant deviations of the heat capacity from the Dulong-Petit law, found in our Monte Carlo computer simulation of the nitrogen cubic gauche polymeric phase [1]. Thermodynamic properties predicted on the basis of this EOS are in good agreement with the experimental data measured at extreme pressures [2]. The possibilities of application of the proposed EOS to other substances, with polymerization of the molecules at high densities are discussed.
Some Thermal Properties of Yb$_{14}$MnSb$_{11}$ and its Solid Solutions
Yb$_{14-x}$RE$_{x}$MnSb$_{11}$ type (RE- La, Pr, Sm, Gd, Tb, Ho, Lu)

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Data on structure, melting temperatures, density, thermal dilatation of Yb$_{14}$MnSb$_{11}$ and its solid solutions with rare earth elements are presented in this works. Yb$_{14}$MnSb$_{11}$ and their solid solutions are high-temperature, thermoelectrical materials. From the position of thermoelectrical materials thermal stability of these materials is also functional property since the exploitation of the material is carried out under high temperatures, where diffusion, volatility, oxidation processes easily occur. Due to this the results of melting temperature and thermal dilatation of Yb$_{14}$MnSb$_{11}$ and its solid solutions with some RE are presented in the present work. Crystals were obtained by melt-solution method using tin as a solvent. X-ray structural study of single samples was conducted on the apparatus DRON-UM (R=192мм, CuKa-radiation, Ni-filter, scintillation detector with amplitude discrimination, step 0,02° 2q, impulse storage time in each point 3с, room temperature) in the region of angles from 5 to 80° 2q.

1. Thermal stability of crystals was studied by high heating rate thermomicroscopic method analysis and it was found that compound .Yb$_{14}$MnSb$_{11}$ and their solid solutions is melt at decomposition.

2. Density was measured by microburette method using dissolved air free ethyl alcohol as a liquid.

3. Thermal expansion was measured in cylindrical samples about 4 mm in diameter, 10-13mm long the temperature range 25-750°C using a high-temperature dilatometer. Function $\Delta L/L_0 - f(T)$ is linear for all materials that indicate the constant coefficient of thermal dilatation $\alpha$ in this region of temperatures .To obtain information on chemical link stability characteristic temperature Debye and mean-square substitution in crystal were calculated.

Thermal expansion coefficients, melting temperatures and Debye temperatures evidences of changes after composition of RE – 0.45-0.7 characteristics. Probably it can be explained by that fact that solubility limit of RE in this compound switches to this concentration.

Acknowledgements

The work was conducted under financial support of ISTC (project T-2067)
Some Thermal Properties of $\text{Yb}_{14}\text{MnSb}_{11}$ and its Solid Solutions

$\text{Yb}_{14-x}\text{RE}_x\text{MnSb}_{11}$ type (RE- La, Pr, Sm, Gd, Tb, Ho, Lu)

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Data on structure, melting temperatures, density, thermal dilatation of $\text{Yb}_{14}\text{MnSb}_{11}$ and its solid solutions with rare earth elements are presented in this work. $\text{Yb}_{14}\text{MnSb}_{11}$ and their solid solutions are high-temperature, thermoelectrical materials. From the position of thermoelectrical materials thermal stability of these materials is also functional property since the exploitation of the material is carried out under high temperatures, where diffusion, volatility, oxidation processes easily occur. Due to this the results of melting temperature and thermal dilatation of $\text{Yb}_{14}\text{MnSb}_{11}$ and its solid solutions with some RE are presented in the present work. Crystals were obtained by melt-solution method using tin as a solvent. X-ray structural study of single samples was conducted on the apparatus DRON-UM (R=192мм, CuKa-radiation, Ni-filter, scintillation detector with amplitude discrimination, step 0,02° 2θ, impulse storage time in each point 3с, room temperature) in the region of angles from 5 to 80° 2θ.

1. Thermal stability of crystals was studied by high heating rate thermomicroscopic method analysis and it was found that compound $\text{Yb}_{14}\text{MnSb}_{11}$ and their solid solutions is melt at decomposition.

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Thermal expansion coefficients, melting temperatures and Debye temperatures evidences of changes after composition of RE – 0.45-0.7 characteristics. Probably it can be explained by that fact that solubility limit of RE in this compound switches to this concentration.

Acknowledgements

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Determination of Heat Capacity by means of Longitudinal Guarded Comparative Calorimeter - Correction Methods

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Even though Differential Scanning Calorimetry (DSC) is a common method for the determination of specific heat capacity, there is also need for methods suitable for a larger specimen size in the range of several cubic centimeters instead of micro liters. For phase change materials or compounds which show specimen size dependent thermophysical caloric properties below a critical specimen volume, e.g. sub cooling effects, the larger specimen volumes are absolutely essential. The Longitudinal Guarded Heat Flow Method is a well-known steady state method to measure the thermal conductivity of medium sized solid samples. With a modification of the measurement procedure to a transient temperature step at the top and bottom end of the stack it is now possible to determine the heat capacity of a specimen in a defined temperature interval. An apparent heat flux is determined during the transient heating phase. Numerical simulations of this new procedure are presented and discussed. The simulations indicate that, due to the transient nature of the technique, a correction in respect to the heat capacity of the reference specimens has to be applied to the measurement data. For this task a novel analytical method is provided. A correction factor is introduced which only depends on the geometry of the experimental setup. This analytical method is validated by numerical simulations. The results show good agreement and recommend the proposed method for the practical use.
Testing the Accuracy of the Soft-SAFT Parameterization: Simultaneous Description of Phase Equilibria and Derivative Properties

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Although it is of common practice to remark the theoretical background of statistical mechanics based equations of state (EoS), such as the family of SAFT EoSs, these approaches are not always used in a systematic and predictive manner becoming, in some occasions, to behave similarly to any correlation. The ability to describe polar and hydrogen bonding systems in wide ranges of thermodynamic conditions is undoubtedly a step forward in the thermodynamic modelling for industrial applications, but unfortunately most studies are limited to phase equilibria calculations. The so-called predictability and transferability of the SAFT molecular parameters should be given by the ability to describe other properties, such as heat capacity, isothermal compressibility and speed of sound. In some cases, different sets of molecular parameters offer a similar description of the phase envelope, while having a very different performance when studying derivative properties. In this work, we propose to test the soft-SAFT EoS to describe the phase equilibria and derivative properties of a series of systems, including alkanes, alcohols, carboxylic acids and ionic liquids. Apart from the classical parameters optimization method, where only density and vapor pressure data are used, a new method for determining the soft-SAFT compound parameters, including derivative properties data, is investigated and developed. A discussion about the most relevant thermodynamic properties to be included in the parameters fitting, their weight in the regression procedure and the influence of the association molecular parameters in the families where short-range interactions are present will be carried out. Since advanced association EoSs generally derive from the same theoretical background, the methods and conclusions developed can be easily transferred to other SAFT models.
Vapor-Liquid Equilibria and Water Activities of Aqueous Ionic Liquids with the Soft-SAFT EoS

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The unique physical properties of ionic liquids (ILs) make them valuable alternatives to traditional compounds for different applications. Aqueous ILs systems are of particular interest for different applications such as in absorption refrigeration and in separation and purification processes through the use of aqueous biphasic systems. The precise description of thermodynamic properties and phase equilibria of aqueous ionic liquid solutions is fundamental for a correct design and application of these processes. In this work, the soft-SAFT equation of state (EoS), a successful approach able to accurately describe the thermophysical properties and phase behavior of ILs and their mixtures, will be used to describe water activities and the vapor-liquid equilibrium (VLE) of a wide range of water + IL systems covering different families of ILs. The correct description of these properties provides new insights about aqueous ILs ideal behavior and solute-solvent interactions, and allows further model application to predict the behavior of other aqueous ILs. The information obtained will be used to discriminate among different sets of molecular soft-SAFT parameters for the ILs which have never been modeled using soft-SAFT.
Perfluoropolyethers are a class of synthetic oils used in a variety of high-temperature lubricant and hydraulic fluid applications [1]. The physical properties of PFPEs that make them excellent lubricants at extreme conditions include their thermal and chemical stabilities and very good cold flow properties [2]. In this work the viscous behaviour of Krytox GPL102 a perfluoropolyether F-(CF(CF3)-CF2-O)n-CF2CF3 (with an average $n = 9.5$ and molar mass 1720 g/mol) has been analysed. A coordinated attempt is being made by several laboratories to measure viscosities on the same sample using six different high pressure instruments: three falling body, one vibrating wire, one rotational and one capillary viscometer. This enables us to check the validity of the different calibration procedures used for measurements of viscous liquids with falling body viscometers. We provide new experimental high pressure viscosities (obtained between 273 and 373, at pressures up to 225 MPa with a maximum viscosity of 4170 mPa·s). This study also reports high-temperature, high-pressure density data from 278.15 to 398.15 K and pressures to 120 MPa. The viscosity and density data were satisfactorily fitted to empirical equations, which can be used to interpolate them within the experimental conditions investigated in this study.

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References
In this work the flow and heat transfer characteristics to Sisko nanofluid over a non-linearly stretching sheet in the presence of thermal radiation included in the energy equation with convective boundary condition is investigated in the concerned study. Our nanofluid model incorporates the influences of the thermophoresis and Brownian motion. A similarity transformation is used to transform the governing partial differential equations to a system of non-linear ordinary differential equations. An efficient numerical shooting technique with a fourth-order Runge–Kutta scheme (RK45) is used to obtain the solution of the boundary value problem. The effects of the power-law index, stretching parameter, the thermophoresis, Brownian motion and thermal radiation parameters on the temperature and concentration fields are analyzed and graphically presented. To see the validity of the present work, we made a comparison with the numerical results as well as previously published work with an outstanding compatibility.
An Equation of State Based upon a Rational Form for the Residual Helmholtz Free Energy

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Chemical process modeling and design requires accurate equations to predict energies, entropies and densities. Cubic equations of state have a simple form that can describe thermophysical properties making assumptions that increase error in the prediction. In other hand, recent multi parametric equations can predict thermodynamic properties with high accuracy by increasing the calculation complexity. This work presents a new equation of state (EoS) having a rational form that can describe properties with accuracy comparable to the best multi-parametric equations with less mathematical complexity. This EoS presents the Helmholtz residual energy as a ratio of two polynomial functions in density (no exponential terms in density are included), which can describe the behavior of pure components. The EoS needs 32 parameters to describe a pure fluid. The EoS can be transformed to describe other thermophysical properties as pressure, compressibility factor, heat capacity and speed of sound.

As one example, this work describes nitrogen data from 66 to 520 K at pressures up to 30 MPa. The equation can predict compressibility factors within 0.02% for temperatures between 130 K and 520 K. For temperatures below the critical point the uncertainty is around 0.05%, and within the critical region the uncertainty is higher. The model estimates saturated densities within 0.05% for temperatures below 125 K. This EoS also describes reported speed of sound and heat capacity measurements within 1% everywhere except the near critical region.
This paper is intent to develop quantitative structure property relationships to estimate occupational exposure limits values. Occupational Exposure Limits (OELs) are representing the amount of a workplace health hazard that most workers can be exposed to without harming their health. There are different OELs such as threshold limit value (TLV of ACGIH), permissible exposure limit (PEL of OSHA), recommended exposure limit (REL of NIOSH) and maximum concentration value in the workplace. A new method for the estimation of properties of pure organic compounds is presented. The model is easy to implement and u
Polymer Dispersed Liquid Crystals (PDLCs) consist of liquid crystal (LC) droplets inside a polymer matrix. The possibility for changing LC alignment in PDLCs with an external electric field (EF) makes them useful in technology. Since LC possesses thermal conductivity anisotropy which can be controlled by an EF, thermal conductivity of PDLCs can also be tuned by an EF. In this work, we have established a relationship between the effective thermal conductivity of the film and the average orientation of the LC molecules which has been described using order parameters [1]. Thermal conductivity of Polystyrene-5CB samples, prepared by solvent induced phase separation technique, is investigated using an adapted Photothermal Radiometry technique [2]. The results show that the thermal conductivity of PDLC films depend on the amplitude and frequency of the EF. These behaviors can be explained by the reorientation of the LC molecules inside the droplets and by the effects of depolarization field, described by the Maxwell-Wagner-Sillars theory. Finally, the experimental results give information on electrical properties and elastic parameters of the polymer and LC [3].

References

Defect Motion and Annihilation in Block Copolymer Thin Films

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Using self-consistent field theory and computer simulation of a soft, coarse-grained particle model we study defect motion and annihilation in thin films of lamella-forming block copolymers on neutral and chemically patterned substrates. By virtue of the strain-field mediated interactions, dislocation defects with opposite orientation move towards each other. This motion depends both on the thermodynamic, strain-field mediated driving force and the single-chain dynamics that is required to alter the morphology and reduce the distance between the defect cores. This interplay results in a qualitative dependence of the time evolution on the topology of the defect morphology. Upon collision of the defects, they either spontaneously annihilate or form a metastable, tight defect pair. In the latter case, a free-energy barrier has to be overcome to finally produce a defect-free structure. Computing the minimum free-energy path within self-consistent field theory we investigate the dependence of the free-energy barriers of defect motion and annihilation on incompatibility, strength of the chemical surface pattern, and defect morphology.
Composition-Curvature Coupling in Binary Lipid Membranes

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The coupling between local composition fluctuations in binary lipid membranes and curvature affects the lateral membrane structure. It can result in the formation of spatially modulated stripe phases and has been implicated in the formation of lipid rafts. We propose an efficient method to compute the composition-curvature coupling in molecular simulations and apply it to two coarse-grained membrane models—a minimal, implicit-solvent model and the MARTINI model. Both the weak-curvature behavior that is typical for thermal fluctuations of planar bilayer membranes as well as the strong-curvature regime corresponding to narrow cylindrical membrane tubes are studied by molecular dynamics simulation. The simulation results are analyzed by using a phenomenological model of the thermodynamics of curved, mixed bilayer membranes that accounts for the change of the monolayer area upon bending. Additionally the role of thermodynamic characteristics such as the incompatibility between the two lipid species and asymmetry of composition are investigated.
In this talk we are going to present the conductivity relaxation measurements of a number of ionic liquids (ILs). The dielectric studies of conductivity relaxation were performed as a function of both temperature and pressure. In addition we carried out PVT measurements for all investigated ILs. By combining these two sets of data we were able to analyze density dependence of the conductivity relaxation times and consequently to test the validity of density scaling concept. Moreover the temperature-volume data were analyzed in term of the modified Avramov model. As a result it was pointed out that there is the relation between the electrical transport properties of investigated ILs and their thermodynamic properties, represented by scaling exponent $\gamma$ and Grüneisen constant $\gamma_G$, respectively.
Interfacial Properties of Linear-Cyclic Polymer Blends

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Dynamics of polymers in the melt state is strongly influenced by molecular architecture [1-4] and it is a subject of both industrial and fundamental interest in polymer physics and rheology. Theoretical and computational studies of pure (CPs) and linear (LPs) polymers have been intensively performed in the last decades, however linear-cyclic polymer blends (LCBs) have not been scrutinized to the same depth so far. These polymer systems are important because most experimental data on pure CPs are “contaminated” by the presence of LPs (mainly due to limitations in the purification methods), and the dynamics of LCBs is extremely sensitive to the concentration of LPs. Moreover, blending polymers with different molecular topologies could also be relevant to control interfacial segregation so to avoid macroscopic phase segregation of the polymer film, and providing optimal mechanical properties for a number of polymeric materials used for industrial applications [5,6]. In our brief presentation, we will show some results of a systematic study of bead-spring models of LCBs by means of molecular dynamics simulations. These results are also obtained by changing the nature of the interface and considering the adsorption of the system on a solid substrate (flat wall). We will discuss our findings in the light of theoretical evidences suggesting that cyclic chains segregate to the surface by maximizing the conformational entropy of the system [7], and experimental results providing evidence of the contrary, i.e. cyclic chains are depleted at the film surface [8].

References

Solubility of Carbon Monoxide in Different Bio-Oil Components

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Solubility of Carbon monoxide have been determined in five different bio-oil components namely crotonaldehyde, diacetyl, methylfuran, allyl alcohol and furan at three different temperatures 273.15, 298.15 and 323.15 K and the pressure range from 1 to 7 MPa. The measurements were carried out using static analytic VLE (vapor-liquid equilibrium) cell equipped with ROLSI™ (Rapid Online Sampler Injector) sampler connected to a Gas Chromatograph through heated transfer line. PC-SAFT EOS was employed to model the acquired data. Pure component parameters of the PC-SAFT \((m, \epsilon, \sigma)\) of the bio-oil components were calculated by a simultaneous regression of vapor pressure and liquid molar volume data using Aspen Plus®. Binary Interaction parameters for PC-SAFT have also been regressed. Carbon monoxide solubility in all cases was found to be very low.
A new Single-Sinker Magnetic Suspension Densimeter for Cryogenic Liquid Mixtures and First Results for a Liquefied Natural Gas (LNG) Mixture

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A special densimeter has been developed for accurate measurements of the \((p, \rho, T, x)\) behavior of liquid mixtures at cryogenic temperatures, e.g., liquefied natural gas (LNG). It covers the density range from \((10\) to \(1000)\) kg × m\(^{-3}\), thus enabling density measurements in the homogeneous liquid region, along the saturated liquid line, in the supercritical region and in the homogenous gas region. To realize measurements in the homogeneous liquid, a supercritical liquefaction procedure was established, and a special VLE-cell was implemented. The apparatus is designed for measurements in a temperature range from \((90\) to \(290)\) K at pressures up to \(12\) MPa. The densimeter is based on the Archimedes (buoyancy) principle and is a single-sinker system incorporating a magnetic suspension coupling, which is used at cryogenic temperatures for the first time. This circumstance required the investigation of the force transmission error of the magnetic suspension coupling at low temperatures, and this will be discussed in further detail. Densities can be obtained directly without the need for calibration fluids. The relative combined expanded uncertainty \((k = 2)\) for density measurements in the homogeneous liquid (including the contribution resulting from the uncertainty of the sample gas analysis) is estimated to be approximately \(0.05\) %. We will report first results for a selected synthetic LNG mixture obtained at temperatures \(T = (115, 120,\) and \(125)\) K with pressures up to \(6.5\) MPa. The experimental results are compared to the GERG-2008 reference equation of state for natural gases, which performed very well. Moreover, we will discuss future improvement activities to reduce the overall measurement uncertainty of our instrument.
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New Apparatus for Measuring Interfacial Properties of Fluids at Reservoir Conditions

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Interfacial phenomena are ubiquitous not just in the chemical engineering field, but also in hydrogeology and biotechnology. The efficiency of processes such as enhanced oil recovery (EOR) and carbon capture and storage (CCS) relies greatly on a thorough understanding of interfacial properties such as interfacial tension (IFT) and contact angles (CA) between fluids and solid surfaces. It is already known that factors such as temperature, pressure, and concentration (i.e. for saline solutions and/or systems containing supercritical CO₂) have significant effects on interfacial properties and thus affect the fluid flows and ultimately the effectiveness of processes such as EOR and carbon storage. Currently there are many experimental techniques used to investigate interfacial properties and, for high-pressure high-temperature (HPHT) conditions, those most commonly employed are the pendant drop and the sessile drop methods using drop shape analysis (DSA). To date, the main concern regarding the data already existing in the literature, for example for CA of CO₂-H₂O/brines-quartz systems is in relation to their very large scatter even at similar/identical conditions. In addition, reliable data for more challenging systems that present greater difficulty in measuring such as CO₂-H₂O/brines-calcite are very scarce. In this work, we present the design, set up and validation of a new apparatus capable of measuring CA at reservoir conditions even for more challenging systems such as CO₂-H₂O/brines-calcite. The acquisition of reliable data for this type of system could help facilitate the further development of carbon storage technologies.
Numerous high-nitrogen compounds have explosive properties and attract great attention in the modeling of new high energy materials with projected properties. Important characteristics of explosives and propellants can be calculated from the enthalpy of formation, which is closely related to the stability and sensitivity of these compounds. The experimental enthalpies of formation for many important high-nitrogen compounds are often unknown or determined with relatively large uncertainties. Today quantum chemical calculations can be used successfully for prediction of thermochemical properties or analyzing of experimental data.

The Gaussian-n family methods (G4 and G4(MP2)) combined with atomization reaction were tested in their possibilities to quantitatively estimate the values of enthalpy of formation. To get the accurate gas-phase enthalpies of formation, the quantum chemical calculations combined with isodesmic reaction scheme were used in this study. A set of internally consistent values of enthalpies of formation of nitrogen-containing compounds has been obtained. Among these are nitro compounds, nitramines, amines, heterocycles, and azides with different architecture and functional groups.

The experimental condensed phase enthalpies of formation and enthalpies of sublimation/vaporization were analyzed based on recommended values of the gas phase enthalpy of formation. In some cases a possible inaccuracy of the experimental values has been suggested. The enthalpies of sublimation or vaporization were estimated by quantum chemical calculations for compounds for which no experimental data are available.
The NASA Marshall Space Flight Center’s electrostatic levitation (ESL) laboratory has been recently upgraded with an oxygen partial pressure controller. This system allows the oxygen partial pressure within the vacuum chamber to be measured and controlled, theoretically in the range from $10^{-36}$ to $10^0$ bar. The oxygen control system installed in the ESL laboratory’s main chamber consists of an oxygen sensor, oxygen pump, and a control unit. The sensor is a potentiometric device that determines the difference in oxygen activity in two gas compartments (inside the chamber and the air outside of the chamber) separated by an electrolyte, which is yttria-stabilized zirconia. The pump utilizes coulometric titration to either add or remove oxygen. The system is controlled by a desktop control unit, which can also be accessed via a computer. The controller performs temperature control for the sensor and pump, PID-based current loop, and a control algorithm. Oxygen partial pressure has been shown to play a significant role in the surface tension of liquid metals. Oxide films or dissolved oxygen may lead to significant changes in surface tension. The effects of oxygen partial pressure on the surface tension of undercooled liquid nickel will be analyzed, and the results will be presented. The surface tension will be measured at several different oxygen partial pressures while the sample is undercooled. Surface tension will be measured using the oscillating drop method. While undercooled, each sample will be oscillated several times consecutively to investigate how the surface tension behaves with time while at a particular oxygen partial pressure.
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The thermodynamics have been playing very important roles in revealing the nature of molecules in solution. However, contrary to the well-developed time-resolved spectroscopy, thermodynamic properties during chemical reactions in solution in a time-resolved manner is still very difficult. Recently our group has been working on time-resolved thermodynamics for a variety of photochemical processes in nano-seconds time range. We used the pulsed laser induced transient grating (TG) for quantitative measurements in time domain. Here we will report on the thermodynamic studies of short lived intermediate species of a biological protein, TePixD. TePixD is a blue light sensor. The photochemistry of TePixD studied by absorption spectroscopy revealed that the spectrum of this protein changes after photo excitation within 100 ps. However, there is no absorption change after this ultrafast reaction. We used the TG technique to reveal the spectrally silent dynamics in nanosecond - second time range, which should be essentially important for the biological function. We succeeded in detecting two spectrally silent reaction phases after the creation of the first intermediate by detecting the volume change, enthalpy change, and the diffusion change, which represents the conformational change occurring far from the chromophore. Furthermore, for characterizing these intermediates, we measured the compressibility, and found that this property is enhanced during the reaction. The physical meaning of this enhancement will be discussed.
A Novel Experimental Technique for Determination of the Instability of Asphaltenes in Crude Oils

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Asphaltenes are well-known for their tendency to precipitate and deposit during production of reservoir crude oils. Asphaltene precipitation determination is a key step in studying the asphaltene deposition problems since precipitation is a necessary condition for the asphaltenes to deposit. The methods developed so far (direct methods) to measure the onset of asphaltene precipitation require a minimum particle size - usually from about 0.5 to 1 µm. This means that asphaltene onset detection by direct methods can only occur after precipitated asphaltenes aggregate to exceed the detection limit. In this work, a novel experimental technique called “Indirect Method” is used for studying asphaltene precipitation on both model oil and real crude oil systems. This method, which is a combination of gravimetric and spectroscopy techniques, is proposed for determination of the asphaltene precipitation onset as well as the amount precipitated. The results obtained in this study show that the indirect method has three main advantages over direct methods. First, it can be applied for determination of both the onset and the amount of asphaltene precipitation. By having a proper calibration curve, the absorbance of the supernatant fluid after centrifugation step, can be easily and accurately related to the amount of precipitated asphaltene. Also, the indirect method can be used for crude oils ranging from very low to high asphaltene content; model oils studied in this work contained 0.1 wt% asphaltenes (considered as a low concentration) to 5 wt% asphaltenes (considered as a high concentration). Finally, the minimum particle size detected with the indirect method is smaller than with the direct methods, making the indirect method more sensitive to the size of precipitated asphaltene particles.
Fe and Ni are important constituents for various industrial alloys such as stainless steels, hastelloy, inconel, permalloy, and inver alloys. Each alloy has an excellent property such as high corrosion resistance, high heat resistance, high magnetic permeability or low thermal expansion coefficient. From the practical importance, thermophysical properties of the Fe-Ni melts should be well established. As a first step, we have studied the density of the melts because the density is the most basic property required for measurements of surface tension, heat capacity, and thermal conductivity. Thus, the purpose of this study is to measure the accurate density of the Fe-Ni binary melts using an electromagnetic levitation technique in a static magnetic field. A static magnetic field was employed to effectively suppress the surface oscillation and translational motion of the levitated sample droplet, which enables a high-precision density measurement. This experimental facility is called PROSPECT, which has been designed to measure heat capacity, emissivity, thermal conductivity, density and surface tension of metallic melts with high accuracy in our laboratory. Using PROSPECT, the volume of the levitating sample droplet was measured from the sample images taken by a high-speed camera with a laser back illumination system. The sample temperature was monitored using a pyrometer, and it was calibrated using the liquidus temperatures of the alloy. The densities were measured from 0 to 100 mol% Fe in the Fe-Ni melts. For all compositions of the melts, the densities are expressed with a linear function of temperature. We also determined the molar volume of the melts as a function of composition. It shows a positive deviation from an ideal solution, which indicates that the excess molar volume is positive over the entire range of composition. Details of experimental procedure, results and discussion will be presented in the symposium.
Up until present, the majority of supercritical applications have used either carbon dioxide or, less frequently, n-alkanes as the principle solvent. The greatest disadvantage with these solvents is their lack of polarity, and consequentially, the poor solvation power. A means to overcome the low solubilities, by improving the polarisability of the solvent, is by the addition of a polar co-solvent to the mixture. These liquid co-solvents must, however, be separated from the solute, making the process more complex. This study investigated the use of trifluoromethane (CHF₃, R-23) and hexafluoroethane (CF₆, R-116) as possible solvents for supercritical extraction, as both have critical temperatures that are close to ambient temperatures and low critical pressures. Trifluoromethane was of particular interest, as it is a highly polar species. High pressure phase equilibria of binary mixtures consisting of (refrigerant + hydrocarbon) were measured using a static analytic apparatus. The data was regressed using the (PR-MC + WS/NTRL) thermodynamic model, and the uncertainties were evaluated using the methods recommended by NIST. The critical loci of the binary mixtures were predicted by the extrapolation of the experimental data. Ternary phase equilibrium data for the mixtures of (n-hexane + n-decane) and (n-octane + n-decane) with (trifluoromethane or hexafluoroethane) were measured. The selectivity of the solvent was determined from the ternary data and compared to the apparent selectivity calculated from the binary data. These curves were then compared against published data for these liquid mixtures in carbon dioxide. The refrigerants appear to have a selectivity similar to that of carbon dioxide for the separation of these components. There is, however, a substantial increase in the solubilities of the n-alkanes in trifluoromethane when compared to those observed in non-polar solvents.
Solubility Correlation of H$_2$S in H$_2$O and NaCl(aq) up to 573 K and 40 MPa

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While the data characterizing dissolution of carbon dioxide in aqueous solutions at geological conditions are numerous much less information is available on solubility of hydrogen sulfide. Yet these data are of high practical interest in connection with removal of H$_2$S from the streams of raw natural gas and its subsequent storage in underground aquifers. In this contribution the selected reliable literature data on solubility of H$_2$S in H$_2$O and NaCl(aq) are used to establish a representative correlation as a function of temperature, pressure and NaCl concentration. The state behaviour of H$_2$S in the vapour phase is calculated from the equation of state by Lemmon and Span (J.Chem.Eng.Data 2006, 51,785) and the Henry’s law constants generated from the SOCW model for hydration properties of H$_2$S(aq) (Majer et al. Fluid Phase Equilib. 2008, 272, 65). The activity coefficients of hydrogen sulfide in pure water and salt solution are expressed by the Pitzer interaction model. The parameters for NaCl(aq) were taken from the review of Archer (J.Phys.Chem.Ref.Data 21, 1992, 793) while those for H$_2$S in binary and ternary solution are newly determined. Since the numeric calculation is rather complex an interactive software is available on internet allowing generation of solubilities and activity coefficients of hydrogen sulfide at a given temperature, pressure and concentration of NaCl.
Isobaric Heat Capacity of Water

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Abstract

Water is an anomalous and unique liquid in the sense that some of its physical properties do not exhibit monotonous behaviour when plotted against temperature. For example, isobaric heat capacity exhibits a minimum near 37 C. No theory/model is available in the literature to explain this behaviour of isobaric heat capacity with temperature. We, therefore, suggest a model to study the isobaric heat capacity of water as a function of temperature. The model is based on two-state theory of water in which water is considered as a mixture of two species. One of the specie is called open-packed specie resembling with ice structure and having mole fraction as X0 whereas the other is called closed-packed species resembling with un-hydrogen bonded water molecules and having mole fraction as Xc=1- X0 .An empirical relation is developed as a function of temperature for open-packed specie using the data reported by Davis and Litovitz [J.Chem.Phys. 42,2563 (1965)]. On the basis of this mixture model, isobaric heat capacity of water is assumed as

\[ \text{Cp}=X_0 \text{Cp}_0+(1-X_0)\text{Cp}_c \]

Further \( \text{Cp}_0 \) and \( \text{Cp}_c \) are considered as a function of temperature. The computation of heat capacity indicates a minimum near 40 C which is in very good agreement with experimental results.
Chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) are being phased out according to the Montreal Protocol. Recently, unsaturated fluorinated compounds known as hydrofluoro-olefins (HFOs) have been proposed as promising refrigerants due to their lower GWPs and short atmospheric lifetime. 2,3,3,3-Tetrafluoroprop-1-ene (HFO1234yf), joint developed by Honeywell and Dupont, has a very low GWP of about 4 and a very short atmospheric lifetime of 0.03 years. It offers similar thermophysical properties to HFC134a, and has been accepted as a alternative refrigerant. In this work, the solubilities of 2,3,3,3-Tetrafluoroprop-1-ene (HFO1234yf) in pentaerythritol tetrapentanoate (PEC5) have been measured from 283.15 to 353.15 K based on the isochoric method. The experimental solubility data were correlated using the Peng–Robinson equation of state with Huron–Vidal mixing rules and the NRTL equation for the excess Gibbs energy at infinite pressure. The absolute average deviation between experimental data and calculated values was 0.86 %, and the maximum relative deviation was 3.23 %.
Temperature Dependency of Interaction Parameters of Electrolyte NRTL Model

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Accurate thermodynamic modeling of aqueous electrolyte solutions is essential for many industrial applications such as hydraulic fracturing, desalination, nuclear waste management, etc. Requiring only two binary interaction parameters, the electrolyte non-random two liquid (eNRTL) model is capable of representing the liquid phase nonideality over the entire concentration range from pure water to pure fused salt. Another important characteristic of the eNRTL model is the weak temperature dependency of the binary interaction parameters. In this study we investigate the relationship between temperature coefficients of the eNRTL binary interaction parameters and excess molar enthalpy of electrolyte solutions. We show excess molar enthalpy of electrolyte solutions form a simple family of curves as function of electrolyte concentration. We further show the temperature dependency of the eNRTL binary interaction parameters can be expressed in a Gibbs-Helmholtz type expression with three temperature coefficients representing Gibbs energy, enthalpy, and heat capacity contributions. The enthalpy term of the temperature dependency expression has been correlated to excess molar enthalpy of electrolyte solutions for more than 100 electrolytes. The resulting eNRTL model and model parameters provide a comprehensive thermodynamic framework to represent all thermodynamic properties of aqueous electrolyte solutions including vapor pressure depression, mean ionic activity coefficients, osmotic coefficients, excess enthalpy, and heat capacity.
Density and Speed of Sound for the Binary System HFE 7500 + Di-Isopropyl Ether

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Hydrofluoroether fluids (HFEs) are being used as third generation alternatives to replace CFCs (chlorofluorocarbons), HCFCs (hydrochlorofluorocarbons) and PFCs (perfluorocarbons) because of their nearly zero ozone depletion, relatively low global warming potential and short atmospheric lifetimes [1]. A variety of HFEs have been synthesized, their performance and environmental properties and hence their utility can vary widely [2]. 2-trifluoromethyl-3-ethoxydodecafluorohexane, known as HFE 7500, is a nonflammable fluid with very low global warming potential for use in heat transfer applications. In addition, it may be industrially used to cool high voltage transformers and power electronics, to cool semiconductor thermal shock and test equipment and as an alternative to commonly used fluids in pharmaceutical and chemical manufacturing processes, such as freeze drying and reactor cooling. To some extent, it can be used in mixture with other solvents. Experimental densities and speeds of sound for the binary system HFE 7100 + di-isopropyl ether have been measured at 298.15 K and at atmospheric pressure. The excess molar volumes and the deviations in isentropic compressibility upon mixing have been correlated by the Redlich-Kister polynomial. No data were found in the literature for this binary mixture. Acknowledgements: N. Muñoz acknowledges support for this research to the University of Burgos, for the funding of her doctoral grant. This work is part of the Doctoral Thesis of N. Muñoz.

References

Characterizing the thermal transport properties of a material requires the knowledge of two independent parameters: thermal diffusivity ($D$) and thermal effusivity ($e$) (or thermal conductivity). The flash method has become a standard one to measure thermal diffusivity. It consists of heating the front face of an opaque plate by a brief light pulse and analyzing the temperature evolution at its rear surface or at the illuminated surface. However, the flash method applied to free standing plates only provides its thermal diffusivity, since the thermal effusivity is correlated to the energy absorbed by the sample surface that cannot be easily determined. To overcome this drawback we propose to bring the rear surface of the plate in contact with a fluid backing. In this way, the front surface temperature will be sensitive to the thermal mismatch between plate and fluid that is governed by their effusivity ratio. Following the idea of using a fluid for thermal contrast, we propose in this work using the flash method in the front configuration to obtain diffusivity and effusivity simultaneously in a fast manner. We have first calculated the front surface temperature of an opaque plate in contact with a fluid after being illuminated by a brief light pulse. The effect of the finite duration of the laser pulse as well as the heat losses by convection and radiation are also included in the model. It is shown that the sensitivities of the front surface temperature to $D$ and $e$ are uncorrelated (non-proportional). Then, in order to verify the validity of the method and to set its application limits we have performed flash measurements, using a pulsed laser and an infrared camera, on several calibrated materials, covering a wide range of thermal transport properties, taking as backing material water and ethanol.
Into the Depths of Deep Eutectic Solvents

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Ionic liquids (ILs) have been successfully tested in a wide range of applications; however, their high price and complicated synthesis make them infeasible for large scale implementation. A decade ago, a new generation of solvents so called deep eutectic solvents (DESs) was reported for the first time. DESs show similar properties to ILs and they have proven to be an excellent alternative to ILs in many applications where ILs succeeded first. Besides, DESs can be prepared easily and cheaply, with low-cost starting materials, no need of solvents, no atom loss during the formation and no additional purification requirements. The main problem that scientists are facing when they want to use DESs in different applications is the lack of information on the fundamentals of these solvents. Why do they form? How do they form? How do the hydrogen bond donor (HBD) and the hydrogen bond acceptor (HBA) interact? How do DESs interact with other compounds? Can we predict their thermophysical properties? The answer to these questions will provide to researchers new insights on the application of these solvents, solving the problem of trial-and-error experimentation. In this work, we present a detailed analysis of molecular interactions and conformational states of two selected DESs: lactic acid – choline chloride (2:1) and glycolic acid – choline chloride (1:1), using density functional theory (DFT) and second-order Møller–Plesset perturbation theory (MP2) with various basis sets. Theoretical calculations were performed using the GAUSSIAN 03 software package. The obtained results are used to evaluate the nature of interactions between the HBD and HBA and their structural features. Additionally, it will contribute to the better understanding of how DESs are formed.
Algae have a variety of uses, including pharmaceutical and cosmetic products. Currently, there are also efforts to provide energy from algal biomass in the form of biodiesel, bioethanol and biogas. To optimize the commercial production and use of algal biomass, production facilities have to be specifically designed to handle the source materials and subsequent products. This requires a knowledge of their thermophysical properties. To that end, density, viscosity, and heat capacity of the marine microalgae *Nannochloropsis salina* were determined experimentally at atmospheric pressure and as a function of temperature and total algal biomass solid content. Density was measured using a vibrating tube densimeter over the temperature range from 293.15 K to 333.15 K. Viscosity was determined via a compact falling needle rheometer from 293.15 K to 323.15 K. Finally, heat capacity was measured with a differential scanning calorimeter over the temperature range from 283.15 K to 333.15 K. The algal samples were measured at ten different total solid contents covering a range from 1.4% to 20.3%. Correlation analyses show a relationship between experimental data, temperature, and total solid content for each of the investigated thermophysical properties. Therefore, equations for calculating these properties as a function of temperature and total solid content were developed. Experimental results, as well as results from the correlation analyses and the developed equations, will be presented.
Effect of Thermophysical Properties of Fluids on Heat and Mass Transfer in Energy Systems

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The main purpose of the present work is a study of the effect of kinematic viscosity, density, conductivity, ion concentration and other properties of electrically conducting fluids (such as solutions of salts and acids, liquid metal coolants etc.) on the vortex motion and swirling of a flow. It was considered an interaction of three factors acting on conductive fluid: constant magnetic field, electric field and swirling of a flow. Presence of two of the three above-mentioned factors leads to appearance of the third. Effects based on interdependency between electrical, magnetic and vortex fields and their influence on velocity flow and heat transfer for liquids with different thermophysical properties were studied. The present research program included development of experimental setup, choice of electrolyte as a modeling liquid, elaboration of techniques for measurement of thermophysical parameters and visualization methods of vortex formation process. Constant magnetic field was created by means of sphere-shape magnet placed in the centre of a tank with electrolyte. Experiments were fulfilled for various solutions of electrolytes. For obtaining of the most precise visualization pictures, the solution of acetic acid was chosen. There were two electrodes under electrical voltage: spherical magnet itself and mobile cylindrical probe having the opportunity to change an angle between probe direction and magnetic axis of sphere. Formation of complicated closed helical vortex structures was visualized in the liquid around the moving probe during the passing of electric current. The physical explanation of the observed processes was proposed on the base of experimental results. The report contains the illustrations demonstrating agreement of proposed physical model of heat and mass transfer with obtained visualization pictures of vortex motion and temperature distributions. Revelation of mechanisms of enhancement of heat and mass transfer in conducting fluids placed in magnetic field is topical for engineering energy systems, such as, for example, nuclear reactors with liquid metal coolants and for prediction of some hazardous geophysical processes such as hurricanes, tornados, tsunami, changing the direction of ocean currents.
When a fluid mixture is subjected to a thermal gradient, it responds with concentration gradients: some species enrich at the cold side of the cell, while some others enrich at the hot side. Once the stationary state is reached, one may define the Soret coefficient that links the mole fraction gradient to the thermal gradient. Recent experimental and molecular simulation works have shown that the thermal diffusion process is sensitive to mass ratio, molecular mass distribution and molecular interactions between different species. Usually, separation effects are small and the Soret coefficient is difficult to predict. Moreover, the importance of molecular interactions between different species was suspected from original works on transport properties and this partly explains why thermal diffusion phenomenon is so difficult to predict. In simple systems (like Lennard-Jones mixtures) it is possible to make a clear link between the thermal diffusion coefficient behavior with composition and thermodynamics properties of the mixture. However, in real applications, the number of species under thermal gradient is often larger than two. From a fundamental point of view, the definition of a Soret coefficient for multicomponent mixtures may be problematic. Also, no practical rule exists to estimate the behavior of species in a ternary mixture A+B+C from the knowledge of A+B, A+C and B+C mixtures. In this work, we will investigate the behavior of simple ternary Lennard-Jones mixtures using non-equilibrium molecular dynamics simulations. Starting from a purely mass ratio effect (isotopic effect in ternary mixtures), we will introduce other effects by changing interaction parameters between species.
Laser Flash of Semitransparent TBCs

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TBCs are applied to protect components of gas turbines from high temperature combustion gases. Typically they are metal-ceramic multi-layers structures made up of a yttria partially stabilized zirconia (7-8 wt.% Y2O3+ZrO2) deposited either by APS or EB-PVD on a high temperature oxidation/corrosion resistant metallic bond coat (BC). The refractory ceramic porous layer can reduce the temperature of the base metal by 30°C to 100°C, depending on the thickness and on specific microstructural properties of the coating. Typically, thermal diffusivity of TBCs is determined by a laser flash apparatus. Unfortunately, ZrO2 is semitransparent to near IR radiation that is typically delivered by the laser in the laser flash equipment. Moreover, the characterization of TBCs at high temperatures is particularly interesting as the typical working temperature of gas-turbine is >1000 °C. At these temperatures heat transfer is no more limited to conduction and the radiative heat transfer becomes paramount. The evaluation of effective heat conduction is carried out in this work by laser flash equipment describing at the same time common practices and countermeasures to minimize the discrepancies from the commonly used models to analyze data. The effects of blackening surfaces and covering them with thin metallic deposits is considered. The role of heat conduction and radiation is also taken into account trying to separate each contribution.
Insights on the Ionic Liquids Structure-Property Relationship
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Ionic liquids (ILs) are composed of ions, and as a result there are a large number of potential compounds to be synthesized by simple structural rearrangements. Able to be either inert, acting only as solvents or designed to actively participate in a large range of chemical reactions, these ionic compounds have often been considered as "green solvents" because of their negligible vapor pressures and, in many cases, low flammability, when compared with common organic solvents. Moreover, the ionic nature of ILs is the main characteristic responsible for some of their most outstanding properties, namely a high ionic conductivity, high thermal and chemical stability, and enhanced solvation ability for a large array of compounds. At the same time, the combination of different ions, sustained by a wide chemical diversity, allows the tailoring of their properties, making them quasi specific fluids for a particular application, thus "designer solvents". Nonetheless and despite the large number of works outing ionic liquids as "designer solvents", the number of studies dealing with their structural design, besides the simple combination of different cations and anions, is, at this point, surprisingly scarce. In this work the understanding of the structure-property relationship will be evaluated and discussed beyond the cation-anion combination. In particular the effect of cation isomerism or quasi-isomerism, the presence/absence of the aromaticity and the influence of the cation's central atom in a large range of physical, chemical and biological properties is presented.

Acknowledgments

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Nonlocal Constitutive Equations for Shear Flow in Fluids with Strongly Inhomogeneous Density and Velocity Profiles

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We present new theoretical expressions for the density, strain rate and shear pressure profiles in strongly inhomogeneous fluids undergoing steady shear flow with periodic boundary conditions. The expressions that we obtain take the form of truncated functional expansions. In these functional expansions, the independent variables are the spatially dependent longitudinal and transverse forces that we apply in non-equilibrium molecular dynamics simulations. The longitudinal force is directed along the y-axis, is composed of one or more sinusoidal components that vary in the y-direction and it produces strong density inhomogeneity. The transverse force is directed along the x-axis, varies sinusoidally in the y-direction and it produces shear flow. The functional expansions define new material properties, the response functions, which characterise the system’s non-local response to the longitudinal force and the transverse force. We find that the longitudinal force, which is mainly responsible for the generation of density inhomogeneity, also modulates the strain rate and shear pressure profiles. Likewise, we find that the sinusoidal transverse force, which is mainly responsible for the generation of sinusoidal shear flow, can also modify the density. These couplings between density inhomogeneity and shear flow are also characterised by non-local response functions. We conduct non-equilibrium molecular dynamics simulations to calculate all of the response functions needed to describe the response of the system for weak shear flow in the presence of strong density inhomogeneity up to the third order in the functional expansion. These response functions are then substituted directly into the truncated functional expansions and used to predict the density, velocity and shear pressure profiles. The results are compared to the directly evaluated profiles from molecular dynamics simulations and we find that the predicted profiles from the functional expansions give excellent agreement with the directly computed density, velocity and shear pressure profiles.
Coal gasification yields synthesis gas, an important intermediate in bulk chemical manufacturing. It is also vital to the production of liquid transportation fuels through the Fischer-Tropsch process and electricity in Integrated Gasification-Combined Cycle power generation. Minerals naturally present in the coal become molten in entrained flow slagging gasifiers. Molten coal ash slag penetrates and dissolves refractory bricks, which leads to costly plant shutdowns. The extent of coal ash slag penetration and refractory brick dissolution are functions of the slag viscosity, operating temperature, and the composition of the coal ash and refractory bricks. We measured the viscosity of several synthetic coal ash slags with a high-temperature rotary viscometer and their fusion temperatures through optical image analysis of ash cones placed in a tube furnace. All measurements were made in a carbon monoxide-carbon dioxide reducing atmosphere. Samples were analyzed using scanning electron microscopy and x-ray analysis to verify their composition and to identify phases that are present. Thermodynamic phase-transition models were used to calculate the critical viscosity temperature based on the coal ash compositions. These values were then compared with those obtained from empirical correlation models based on ash fusion temperatures. An understanding of slag viscosity as a function of ash composition is important to reducing refractory wear in slagging coal gasifiers, an important step in reducing the economic and environmental cost of coal in the production of chemicals and electricity.
Equilibrium Melting of Water and Water +Sodium Chloride in a Novel Peltier-Element-Based Adiabatic Scanning Calorimeter

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Water and sodium chloride form a eutectic system. However, there are in literature only a limited amount of high-resolution thermal data on its phase behavior, although such information is quite relevant, e.g. for food engineering or cryobiology. We present high-resolution enthalpy and heat capacity data on sodium chloride solutions, ranging from pure water to the eutectic composition, in the temperature range between -30 °C to +10 °C. The measurements have been performed by means of a novel Peltier-element-based implementation of the adiabatic scanning calorimeter (ASC) concept [1,2]. The new instrument is capable of achieving, on mg size samples, accuracy (1 to 2 %) close to that of classical adiabatic heat-step calorimeters (on samples of several grams) and very high temperature resolution. ASC relies on the application of constant power to the sample, and measures the resulting temperature rate. This is exactly the opposite as in DSC, where a fixed temperature rate is enforced on the sample by varying the power. ASC leads naturally to high-resolution equilibrium data, in contrasts to inherently rate-dependent DSC data [3,4]. In addition, ASC also measures the enthalpy simultaneously with the heat capacity. We present specific heat capacity and enthalpy data for the melting of the ice and of the eutectic phase transition, around -21 °C. Accurate latent heat values are obtained for both transitions, as well as the melting point depression. A novel approach for purity determination on the basis of the data obtained by pASC will be discussed. These data will be used in a discussion of the colligative nature of the solutions and the dissociation of the salt.

References

Phase Transitions of Binary Lipid Mixtures: a Combined Study by Adiabatic Scanning Calorimetry and Quartz Crystal Microbalance with Dissipation Monitoring

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The interest in lipid phase behavior stems from the nature and the thermodynamics of phase transitions, the mechanisms behind lipid miscibility and lateral phase separation, and the existence of critical phenomena [1]. This requires the knowledge of static and kinetic thermodynamic properties of pure lipids and lipid mixtures. In this work, we study phase transitions of lipid mixtures by means of Peltier-element-based adiabatic scanning calorimetry (pASC) [2-5] and quartz crystal microbalance with dissipation monitoring (QCM-D) [6]. We test the capability of pASC, a novel type of calorimeter, for measuring biologically relevant samples, for which
unambiguous information on thermal properties, namely, the specific heat capacity $c_p(T)$ and the specific enthalpy $h(T)$, is obtained. QCM-D is proposed as a genuine way of determining phase diagrams by analysing the temperature dependence of the viscosity $\eta(T)$. Two binary mixtures of phospholipids with the same polar head and differing in the alkyl chain length, DMPC + DPPC and DMPC + DSPC, are presented. Both techniques give consistent phase diagrams, which compare well with literature results, showing their capability to map the phase behaviour of single lipids as well as lipid mixtures.

References

Melittin Disruption of Raft and Non-Raft-Forming Biomimetic Membranes:
a Study by Quartz Crystal Microbalance with Dissipation Monitoring

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Both bacterial and eukaryotic cell membranes are complex mixtures of lipids whose physical properties vary depending on the composition of the membrane, in particular, on the phase of the constituent lipids. Liquid disordered-liquid ordered (Ld-Lo) lateral phase separation in eukaryotic membranes, i.e., the formation of the so-called lipid rafts, has shown to play an important role in the localization or transport of different proteins [1]. In this work we examine the role of lateral phase separation in cholesterol-containing biomimetic membranes on the disrupting action of Melittin using a label-free surface-sensitive technique, quartz crystal microbalance with dissipation monitoring (QCM-D). Melittin disruption mechanisms depend strongly on the geometry of the lipid layer; however, despite the interplay between layer geometry/thickness and Melittin activity, results indicate that the presence of lipid heterogeneity and lateral phase separation greatly influences the disrupting efficiency of Melittin. In homogeneous non-raft forming membranes with high cholesterol content, Melittin spontaneous activity is strongly delayed compared to heterogeneous raft-forming systems with the same amount of cholesterol [2]. These results are in agreement with fluorescence microscopy studies [3] and confirm the importance of lateral phase separation as a determinant factor in peptide activity. The information provided can be used for the design of more efficient antimicrobial peptides and the possibility of using a label-free approach for tailored-membranes and interactions with other types of peptides, such as amyloid peptides.

References

Correlation of Avocado Oil Content with the Emissivity Measured from the Skin

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In recent years the avocado industry in Mexico has had a strong growth; only in the state of Michoacan are over 9000 Hass avocado producers with a production of 950,942 tons per year. Although most of the domestic avocado production is destined for fresh consumption, there is a certain amount that is for oil extraction. It is still not easy or cheap to determine the amount of oil contributed by each avocado in order to select the best avocados for oil extraction; so far, not there are automatic techniques capable of determining their oil content based on non-invasive, relatively quick, and non susceptible to human errors measurements. Moreover, infrared thermography has demonstrated its ability for the evaluation and characterization of different systems, from solids to biomaterials, observing that vegetal physiological characteristics are possible to measure with this. In this study we proposed the evaluation of oil content in avocados based on non-invasive and non-destructive measurement using infrared thermography. The evolution of the emissivity of avocado will be analyzed in the mid-infrared range by the characterization of thermal images from its skin. Thus, a correlation between the emissivity and the oil content is discussed as well as the evaluation of avocado maturity process.
Effect of VLE Uncertainties on the Design of Separation Sequences by Distillation

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It is widely recognized by experts that the computer-based design of chemical processes depends strongly on the correlated thermodynamic and transport properties, and that the effect of overall property uncertainties should be incorporated into the design. The most significant source of property uncertainties on process design is from the correlations of phase equilibrium. Many approaches have been proposed, but uncertainty analysis is not a routine element of today’s industrial practice, mainly because education and awareness are lacking, and the proposed methods are difficult to apply. In order to help rectify the situation, Mathias [1] developed an intuitive and easy-to-apply method based upon treating the mixture, for the purpose of perturbation, as a set of pseudobinaries described by the Margules equation. Mathias applied his method to two examples – (1) a propylene-propane superfractionator for which small changes in correlated relative volatilities have a large effect on the design of the distillation column; and (2) a dehexanizer column that separates a mixture containing many close-boiling components – and demonstrated that the proposed methodology provides quantitative insight into the effect of property uncertainties and helps to quantify the safety factors that need to be imposed upon the design. In this presentation the Margules perturbation method is applied to the “textbook” separation of an acetone-chloroform-benzene mixture; this example was proposed by Westerberg and Wahnschafft [2], and was previously studied by Parodi and Campanella [3]. The approach of Parodi and Campanella uses different levels of data fitting to quantify uncertainties, while Mathias’ methodology is to obtain the best fit of the data, and then apply uncertainties based upon experimental uncertainties and any model inadequacies. Comparison between the two uncertainty-analysis methods enables better understanding of the use of uncertainty analysis in the industrial practice of process engineering.

References

Processes to reduce the CO$_2$ content of natural gas typically produce two product streams: a Sales Gas with low CO$_2$ content and a CO$_2$ Product with high CO$_2$ content. An important design question is to what extent the water content must be reduced to in order to ensure that hydrates do not form in pipeline transportation of the two products. Since there is considerable disagreement in the available data for the water solubility in CO$_2$, a round-robin data program was structured by Fluor Corporation to accurately establish the water solubility. Song and Kobayashi measured the water content of natural gas and NGL in an extensive research program for GPA over more than a decade, and GPA RR-99 [1] presents their measurements in the CO$_2$-rich phase. The experimental data of Song and Kobayashi indicate a strong pressure dependence of the water solubility. On the other hand, Seo, Kang and Lee [2] measured data in the relatively high-temperature region (274 to 294 K) and concluded that the pressure dependence of the solubility is weak. The strong pressure dependence of the Song and Kobayashi data was also questioned using a theoretical basis by Li, Jakobsen and Stang [3] and Mathias [4]. Since the data are extremely important to process design, Fluor solicited proposals for a round-robin data program to measure the equilibrium water content in CO$_2$ at low temperature (down to 228 K) and high pressures (172 to 276 bar). Two laboratories were chosen to independently make the measurements, and the results will be presented at the Nineteenth Symposium.

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Material Emissivity Determination by Virtual Source Method in Temperature Applications

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Precise and reliable methods for material properties determination have played an important role in many fields of science. Emissivity as one of the material properties is important for temperature metrology and more specific for the radiation thermometry measurements. Without the precise and reliable knowledge of material emissivity it would be difficult to determine the precise temperature of a surface with confidence. Radiation thermometry techniques are used in many industrial applications for temperature determination where contact measurements cannot be used. Non contact measurements of temperature bring many advantages with them compared to contact methods, but still even through great deal of improvement in the recent years still many issues remain that decrease the precision and reliability of these measuring methods. Two fundamental issues associated with the use of radiometric techniques for temperature measurements occur. The first is the unknown emissivity of the object which is necessary to subsequently determine the object’s true surface temperature, and the second is the influence of background radiation from nearby objects and the emission from and absorption by the environment. These issues significantly influence the radiation reaching the detector and the resulting temperature reading. One of the problematic areas that we are going to concentrate on is the determination of emissivity of an unknown material. Commonly used procedures for emissivity determinations are based on knowledge of surface temperature, comparison with a material with a known emissivity, radiometric method and table values for specific material. This paper is going to present a procedure of emissivity determination of a material sample without taking into account the temperature of the sample itself, comparison with a material with a known emissivity or table emissivity values. The principles, results, real application and comparison of this “virtual source method” with previously used methods are presented in the following sections of the paper.
The Thermodynamics of Pelagic Bacteriophage Communities

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We describe measurements from a differential calorimeter capable of measuring the small amounts of heat produced by marine microbes and viruses at natural concentrations. Our measurements show that heat production in the presence of viruses is an order of magnitude larger than in their absence. This increased heat output occurs despite a net decrease in the number of microbes. This provides direct evidence for top-down control of microbial populations by viruses. A comparative statics model predicts that approximately 25\% of the total heat production during the growth phase of a pelagic microbial community is due directly to viral activities. Our results have implications for the energy budget of our planet and for climate prediction.
Thermal Radiative Properties of Refractory Ceramics Materials

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Refractory ceramics materials are widely applied in industry because they are capable of maintaining physical and chemical stability at high temperatures. Thermal radiative properties of ceramics, especially in the near- to mid-infrared region, play an important role in heat transfer analysis and temperature measurement. There is a lack of systematic study of the thermal radiative properties of ceramic materials, due to the complexity of their intrinsic and extrinsic structures. Here, intrinsic structures refer to the crystal structure and chemical composition while extrinsic structures refer to the grain size, porosity, surface roughness, etc. The objective of this study is to correlate the radiative properties of ceramics with their chemical compositions, porosity, grain size, and surface roughness. The ceramics samples considered here include alumina (Al₂O₃), silicon carbide (SiC), and silicon nitride (Si₃N₄). The directional-hemispherical reflectance spectra of selected ceramics samples are obtained at room temperature using Fourier transform infrared spectroscopy (FTIR) and monochromator combined with integrating spheres. The measured wavelengths range from 0.4 μm to 15 μm. In the theoretical analysis, refractive indices of highly dense and porous ceramics are obtained based on the effective medium approximation (EMA). Combined with the Mie scattering theory, the radiative transfer equation (RTE) can be solved using a Monte Carlo ray tracing algorithm, which enables the spectral reflectance prediction. This study will help the understanding of the effects of intrinsic and extrinsic structures on the spectral radiative properties of ceramics.
Effect of Reynolds Number on Deposition of Endothermic Hydrocarbon Fuel in Inside Wall of the Pipe

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Endothermic hydrocarbon fuel has been used as an aircraft and engine coolant for decades. However, coking occurs with heating fuel. Most researches on the deposition have concerned on the effect of the dissolved oxygen, the fuel temperature, the chemistry of deposition and deposit model in recent years. Obviously, the fluid flow and flow mode have a significant effect on deposition of endothermic hydrocarbon fuel in inside wall of the pipe. In view of the literatures, the conflict result on the deposition changed with Reynolds number flowing inside the pipe, some reported the deposition increases with Reynolds number, the others gave opposite result. Thermal stressing of endothermic hydrocarbon fuel RP-3 and JP-10 have been carried out in an isothermal flow reactor when the fuel flow through the stainless steel (0.085 in.-i.d, 0.125 in.-o.d. ss316) pipe. The test temperature and pressure are between 150-200$^\circ$C and up to 2.5MPa, respectively. The deposition was only contributed from the single-phase autoxidation. Reynolds number varied only by changing mass flow rate of studied fuel. Deposition rates on the inside wall of the pipe were measured by using carbon burn-off. The results obtained show deposition rate of RP-3 and JP-10 increase with the Reynolds number in the experimental temperature range. An empirical equation for predicting the effect of Reynolds number on deposition is proposed based on the experimental data in this study. Moreover, we established a mathematical model to describe the experimental process using the computational fluid dynamics (CFD) base on simplified global chemistry model. Simulation results are compared with the experimental data, and it is sure that the new model can calculate the deposition rate of endothermic hydrocarbon fuel in inside wall of the pipe at different flow rate.
Transport, optical thermodynamic and an interfacial (surface tension) property have been computed for three binary and one ternary system (2-propanol + tetrahydrofuran + 2,2,4 trimethylpentane and its constituent binaries) at 4 different temperatures ranging between 298.15 and 323.15 K. Viscosity, the most important transport property, having vast significance in industrial applications especially design calculations, has been computed by employing more than 10 approaches. These include empirical, semi-empirical, correlative and predictive methods. Refractive index, an optical and transport property of importance has also been computed by using 10 approaches. A new approach has been put to test for computing the refractive index for binary systems and has been extended for ternary system under investigation. Surface Tension, an interfacial property has also been computed. Further, excess Gibbs free energy of activation of viscous flow ($\Delta G^*$) has also been elucidated to predict the nature of interactions for all the four systems to get a better understanding of the various intermolecular interactions taking place thereof. The results obtained are compared with the experimental findings taken from literature and a comparative study has been carried out regarding the merit/demerits of the various approaches used for the present investigation. Good agreement with the experimental data is observed. An attempt will also be made to compute thermodynamic properties from literature data.

References

Viscosity Study of Hydrocarbon Liquids at Extreme Conditions

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New experimental data on the viscosity of pure n-octane, isoctane, cyclooctane, squalane, and the binary mixture cyclohexane/n-hexadecane are presented at temperatures up to 523 K and pressures up to 242 MPa. These extreme conditions are representative of those encountered in ultra-deep formations such as in the Gulf of Mexico. The measurements were taken with a novel, variable-volume, windowed Inconel rolling-ball viscometer designed by our team and calibrated with various hydrocarbon fluids over wide ranges of temperature and pressure. The estimated accumulated uncertainty in the reported viscosity data is 3 % at a 95 % confidence level. The reported viscosity results are in good agreement with limited lower temperature, lower pressure literature data. The results are modeled with numerous viscosity models suitable for incorporation in compositional reservoir simulators that are capable of estimating viscosity of multiple-component mixtures of changing composition, such as the correlations of Chung-Lee-Starling, Lorenz-Bray-Clark, Pedersen et al., and Aasberg-Petersen et al. Several less common used but more accurate viscosity models were also considered; including free volume theory and friction theory models. Because density input is required for some of the viscosity models, density was estimated with several equations of state; including the Peng-Robinson (PR), the perturbed-chain, statistical associating fluid theory (PC-SAFT), and two models developed by our team; the high temperature-high pressure, volume-translated Peng-Robinson equation of state (HTHP VT-PR) EoS, and the HTHP PC-SAFT EoS. The free volume theory, used in conjunction with either HTHP density model, appears to give the best results.
Thermodynamic Properties of the Fluorinated Olefin R-1234ze(Z) from Acoustic Measurements

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The speed of sound in gaseous cis-1,3,3,3-tetrafluoroprop-1-ene (R1234ze(Z)) has been determined at temperatures between 305 K and 405 K and at pressures up to 1.8 MPa from measurements of the acoustic and microwave resonance frequencies of a small volume (268 cm³) quasi-spherical resonator. Ideal gas heat capacities and acoustic virial coefficients have been directly interpolated from the data. The coefficients of a virial equation of state were obtained from the acoustic data by modelling the intermolecular potential with a hard-core square-well.
Phase Behaviour of (Propane + H₂O + NaCl): a Study at Reservoir Conditions

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Abstract:

Technical challenges and safety aspects in measuring the phase behaviour of impure CO₂ mixed with reservoir fluids (hydrocarbons and brines) are numerous. To accommodate these, a new semi-analytical apparatus have been developed to operate safely at reservoir conditions with flammable, toxic and sour gases (including SO₂ and H₂S). The new apparatus has a maximum working pressure of 70 MPa and a maximum working temperature of 473 K, thus unlocking the limitations in temperature and pressure that can be found in the literature. The system is equipped with a novel sampling system for the aqueous phase, coupled with an online gas chromatograph fitted with both thermal-conductivity and flame-ionization detectors. All wetted metallic parts are made of titanium and the entire equipment fits within an extracted enclosure where it can be operated under remote control. This work focuses on the VL and LL phase equilibria of propane with NaCl(aq) at molalities of (0, 1.5 and 3.5) mol·kg⁻¹. This system has been studied at temperatures from (273 to 453) K and at pressure from (0.5 to 19) MPa for the propane-rich phase (gas or liquid) and from (0.5 to 70) MPa for the aqueous phase. The experimental results are compared with the few data available in the literature data and with thermodynamic models.

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In this study, the behaviour of derivative properties estimated by equations of state, including isochoric heat capacity, isobaric heat capacity, speed of sound and the Joule-Thomson coefficient for pure compounds and a mixture, have been investigated. The Schmidt-Wagner and Jacobsen-Stewart equations of state were used for predictions of derivative properties of ten different pure compounds from various nonpolar hydrocarbons, nonpolar cyclic hydrocarbons, polar compounds, and refrigerants. The estimations were compared to experimental data. In order to evaluate the behaviour of mixtures, the extended corresponding states principle (ECS) was studied. Analytical relationships were derived for isochoric heat capacity, isobaric heat capacity, the Joule-Thomson coefficient, and the speed of sound. The ECS calculations were compared to the reference surface data of methane + ethane. The ECS principle was found to generate data of high quality.
Advances in computer technology make it possible to determine thermophysical properties of simple molecular fluids with high accuracy entirely from theory. For very low and very high temperatures and also for highly corrosive or toxic substances, \textit{ab initio} approaches represent a reasonable way to obtain accurate values for thermophysical properties. Virial coefficients of gaseous and supercritical fluids up to high order can be calculated using the Mayer-sampling Monte Carlo procedure of Singh and Kofke [1]. For carbon dioxide, a virial equation of state up to eighth order will be presented. A highly accurate \textit{ab initio} two-body potential [2] and a new \textit{ab initio} nonadditive three-body potential were used for the Mayer-sampling computations. Both the two-body and the nonadditive three-body potential are based on counterpoise-corrected supermolecular calculations at the CCSD(T) level of theory. The quadratic Feynman-Hibbs modification to the pair potential [3] was used to account for quantum effects. The resulting virial equation of state will be compared with the best experimental $p\rho T$ data for gaseous and supercritical carbon dioxide.

References

The behavior of different synthetic liquefied natural gas (LNG) mixtures was measured in the temperature range from (105 to 135) K at pressures up to 9 MPa utilizing a single-sinker magnetic suspension densimeter for cryogenic liquid mixtures. Due to the supercritical liquefaction procedure and the integration of a special VLE-cell it was possible to measure (p, ρ, T, x) data in the homogeneous liquid phase of LNG without changing the composition. The mixtures were prepared gravimetrically and then analyzed by gas chromatography at the Dutch metrology institute. The relative combined expanded uncertainty (k = 2) in density considering all effects, including the uncertainty in composition, was approximately 0.05 % for all measurements. Comparisons of our experimental data to the GERG-2008 equation of state for natural gas mixtures revealed clear and systematic deviations up to 0.15 %; in general these deviations increase with decreasing pressures. Anyhow, the reported uncertainty for the GERG-2008 equation is (0.1 to 0.5) % for the conditions considered in the present work, and all measured densities are represented well within this uncertainty range. We also present comparisons to density calculation methods often used in LNG industry such as the Revised Klosek and McKinley Method as well as the COSTALD correlation. These comparisons yield the conclusion that the performance of widely used density calculation methods clearly depends on the pressure range and on the composition of the investigated LNG mixture. This conclusion will be discussed in detail.
Group Contribution Model for Predicting Critical Volume with the Flory-Huggins Theory Asymptotic Behavior

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An assumption that has been made by the BYU DIPPR 801 staff in estimating property values for large molecules is that all families eventually converge to the n-alkane family with increasing chain length. For this purpose, much effort has gone into examining the n-alkane family. Specifically, the properties of n-alkanes as the carbon number approaches infinity have been studied to establish asymptotic convergence to other families. Since the critical point is an essential value for many predictive methods of thermophysical and transport properties, it is particularly important to the DIPPR 801 database. Historically, group contribution (GC) models for predicting the critical volume (VC) have assumed a constant contribution from each functional group. This assumption mathematically renders a critical density curve as a function of carbon number that monotonically increases until reaching a limiting value. However, in 1990 Teja reported an experimental maximum in critical density followed by a decrease for the n-alkane, 1-alkene, and 1-alcohol families. Siepmann verified this observed phenomenon by performing Gibbs Ensemble Monte Carlo simulations on large n-alkanes. With the findings of Teja and Siepmann, new prediction models needed to be developed. However, currently there exist two accepted models for predicting VC that have fundamentally different limiting behaviors that cause the correlations to diverge considerably around C_{20}. This research focuses on simulating molecules large enough to determine the infinite carbon length behavior by performing rigorous nonlinear statistical analysis on a generic VC model. Having concluded which asymptotic trend is correct, a novel GC model was developed to agree with experimental data and the accepted trend. This new model reconciles traditional GC theory with Flory-Huggins polymer theory and provides flexibility when predicting small and large molecules of various families. Model validation is obtained by demonstrating how the new VC model improves liquid density prediction for large compounds.
Low global warming potential (GWP) refrigerant R1243zf is a possible candidate to replace R134a for kitchen refrigerators and air conditioning applications. R1234ze(Z) and R1233zd(E) are very recently under consideration as the candidates to replace R245fa that is widely used in organic Rankine cycles and high-temperature industrial heat pumps. The capillary constant and surface tension of saturated R1243zf, R1234ze(Z), and R1233zd(E) were measured at temperatures from 274 K up to 350 K or the critical temperature, using a measuring apparatus based on the differential capillary rise method. The propagated uncertainty in the surface tension was typically 0.2 mN m\(^{-1}\). The surface tension of R1243zf is approximately 0.5 mN m\(^{-1}\) less than that of R134a at a temperature of 300 K, despite the R1243zf has a higher critical temperature than that of R134a. The surface tension of R1233zd(E) is more than 10% higher than that of R1234ze(E) at a given temperature. The experimentally quantified surface tensions were represented within 0.13 mNm\(^{-1}\) by a van der Waals type equation expressing the temperature dependence as,

\[
s = \begin{align*}
53.30 \times (1 - T_r)^{1.247} & \text{ for R1243zf} \\
56.57 \times (1 - T_r)^{1.22} & \text{ for R1234ze(Z)} \\
61.95 \times (1 - T_r)^{1.277} & \text{ for R1233zd(E)}
\end{align*}
\]

where, \(s\) and \(T_r\) are the surface tension and the reduced temperature, \(T=T/T_{\text{crit}}\). The critical temperatures \(T_{\text{crit}}\) are given as 376.93 K and 423.27 K for R1243zf and R1234ze(Z), respectively, by Higashi et al. (2014, 2013), and 438.75 K for R1233zd(E) by Hulse et al. (2012).
Free Energy Studies of Triethylene Glycol

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Due to the hygroscopic nature of triethylene glycol (TEG) it is commonly used as a dehumidifier in ventilation systems, but it is even more common in industry where it is used both to remove water from natural gas [1], as well as a thermodynamic hydrate inhibitor to prevent the formation of clathrate hydrates [2]. After TEG has been utilized, it is usually regenerated to prevent it from reaching other stages of processing. However, after regeneration, there will inevitably remain trace amounts of TEG. Thus, it is important to gain detailed knowledge on how leftover TEG may affect materials present in later stages of processing. This can be achieved by studying the interface between bulk mixtures (e.g. water and methane) and solid materials of interest, such as calcite (i.e. concrete in pipes), hematite (i.e. rust in pipes), and zeolites (i.e. molecular sieve). Free energy differences and chemical potentials are important tools for investigating the preferred trajectory a physical system will undertake during its lifetime. Therefore, it is of interest to estimate the difference in free energy between TEG on a surface of importance and of TEG in a bulk environment. It is difficult to measure free energies and chemical potentials at the interface between a bulk environment and a surface. Therefore, these properties often need to be estimated using theoretical tools. In our work, we used molecular dynamics (MD) simulations. There exists many methods to perform such estimates from MD data, such as temperature thermodynamic integration, thermodynamic integration and free energy perturbation. These have been considered and the most important have been used to study the free energy of TEG in bulk water and methane.

References

Measurement of the Thermal Conductivity of trans-1-chloro-3,3,3-trifluoropropene (R1233zd(E))

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Halogenated olefins are proposed as alternative refrigerants with near zero ozone depletion potential and reduced global warming potential near one. Thermal conductivity measurements of trans-1-chloro-3,3,3-trifluoropropene (R1233zd(E)) are reported at temperatures from 220 K to 450 K with pressures up to 70 MPa. The properties of R1233zd(E) make it a good candidate for a working fluid in large chillers and as a blowing agent in expanded-foam insulation. The measurements were made with two hot-wire apparatus with platinum wires of 12.7 mm diameter. The measurements were made with the steady-state technique for gas at pressures below 1 MPa, while the transient technique was used for liquid and supercritical gas at pressures above 1 MPa. The low-temperature apparatus was used at temperatures from 220 K to 340 K, while the high-temperature apparatus was used at temperatures above 300 K. The upper temperature and pressure limits of 450 K at 15 MPa were selected based on a series of thermal stability tests that showed signs of decomposition and corrosion at 450 K and 25 MPa. The thermal conductivity data in the critical region show contributions from the thermal conductivity critical enhancement. The critical enhancement for the thermal conductivity of this fluid is consistent with mode-coupling theory that indicates the thermal conductivity of a pure fluid is divergent at the critical point.
The overwhelming scientific and techno-economic analysis has the consensus that aqueous mono-ethanol amine (MEA) scrubbing techniques significantly penalizing the energy sector for CO₂ capture both in combustion processes. Studies have shown that ionic liquids are very promising alternative capture solvents for CO₂ and other toxic gases since; their physical and chemical properties at various temperatures could be adjusted through modifying their cationic and anionic moieties. Additionally, extremely low vapor pressures, high thermal and chemical stability, non-flammable nature, high solvation capacity, and promising gas solubility features, ionic liquids have emerged as attractive compounds since the last decade. Moreover, modifying solvent properties at room temperature through hydrogen bond donors, ionic liquids mixtures may have great potential for efficient CO₂ absorption. Since, mixing two or three components capable of intermolecular interactions through the hydrogen bonding generate deep-eutectic solvents (DES), with depressed freezing point and other eutectic physical properties that lie well below each of the individual constituents of the mixture. DES compounds can be easily prepared with high purity unlike ionic liquids and choice of the additional solvent help to further tune the properties and produce novel compounds with considerable low cost, less or even none toxicity and biodegradable nature. Based on advantageous features, we report preparation of novel deepest melting point eutectic solvent prepared from non-toxic choline chloride and levulinic acid. The initial findings have indicated that, this novel DES has extremely low melting point, strong thermo physical stability and appreciable CO₂ capturing capacity. TGA, FTIR, viscosity, density, pH, and thermal conductivity analysis have also indicated the suitability of this material for CO₂ and other gases solubility. Moreover, the repeated use of material at various temperature and pressure without any decrease in CO₂ capturing capacity makes this material capable to be considered for further investigation on larger scale applications.
The control and characterization of radioactive waste packages coming from the decommissioning of nuclear facilities are a great concern for the management of the repository sites dedicated to these specific wastes. One of the key parameters, in particular for the underground installations, is the control of the thermal power released by the radioactive waste packages. Once they are stored deep underground, they can cause an increase of the surrounding rock temperature that could induce a modification of its containment capabilities over time. It is thus essential to accurately know the thermal activity of waste packages in order to select the suitable storage mode, and to ensure that wastes comply with the requirements defined by the safety authorities in term of thermal power. The French National Agency of Radioactive Waste Management (Andra), which is in charge of all the tasks related to radioactive waste management in France, needs to measure the thermal power of these wastes (with an uncertainty lower than 5 %) by using a reliable measurement method that is traceable to the international system of units (SI). In the framework of the European project “Metrology for decommissioning nuclear facilities”, LNE and Andra work in the development of two prototypes of calorimeter in order to accurately measure the thermal power (up to 500 W) of real size radioactive waste packages. The selected metrological approaches are based on the principles of air circulation calorimeter and heat-flux calorimeter. This paper describes in details the calorimeter prototypes as well as the design of radioactive waste package simulators. First results obtained on the calibration of the calorimeters and on the determination of the thermal powers are presented.

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Calculations of Virial Coefficients and Free Energies

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In the gas phase and supercritical region, thermodynamic properties of substances may be most efficiently
calculated from a virial expansion of the pressure in powers of the density. The $N$'th virial coefficient $B_N$ that
occurs in this expansion is calculated from the intermolecular potential for clusters containing 2 to $N$ molecules.
The computational cost of a direct calculation of $B_N$ scales worse than factorially with $N$, and the feasibility limit of
direct calculations is $N=8-10$, which can be insufficient in the supercritical region. The author recently devised a
new method of calculation which scales only exponentially with $N$, making calculations up to $N=15$ possible. The
method appears to be numerically stable, and can be applied without extra cost to non-pair-additive potential
energy functions. In the liquid phase, free energies relative to the ideal gas reference are more difficult to
calculate. Promising results have been obtained for realistic molecular models using nested sampling (also known
as energy partitioning), which calculates the density of states directly relative to the ideal gas. This allows the free
energy to be calculated as a function of temperature from a single simulation. The nested sampling method can be
used to calculate thermodynamics of liquid mixing and of the liquid-gas phase transition, and recent work has
enabled the calculation of free energies for solids, and thermodynamic properties of solid-liquid equilibria.
The speed of sound of deuterium oxide (heavy water, D₂O) was measured over the temperature range of (278.15 to 353.15) K with pressures up to 20 MPa utilizing the double-path length pulse-echo technique. The sound waves were propagated by a piezo transducer operated at high frequency, which was used both as emitter and receiver. Measurements were carried out using a single-burst method, whereby the echo signals were recorded with a digital oscilloscope and then loaded to a computer. Subsequently, the first echo signal of each path length was identified and processed by a special software data analysis tool, and the time of flight was computed. This single-burst method in conjunction with the new data analysis tool helped us to improve the reproducibility of the measurements and thus decreased the overall experimental uncertainty. The speed of sound system was calibrated with pure water at temperatures between $T = (274.15$ and 353.15) K and ambient pressure. The reference equation of state for ordinary water represents the calibration data within the uncertainty of the equation of 0.005 %. The relative combined expanded uncertainty ($k = 2$) in speed of sound for the measurements with deuterium oxide was 0.02 % over the entire temperature and pressure range. Comparisons of the measured sound speed data with other experimental data from literature and values calculated from a new reference equation of state for heavy water will be presented.
Enhanced Heat Transport in Nanoscaled Copper Reinforced PANI Nanocomposites

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The conducting Copper/Polyaniline nanocomposites are synthesized with the help of in-situ oxidative polymerization of aniline in the presence of copper nitrate as precursor. The Potassium Bi-iodate is used as oxidant material. The morphological characterization of as synthesized Cu-PANI nanocomposites confirms the formation of copper nanoparticles covered with Polyaniline nanoscaled fibril structures. The structural characterization like XRD of as synthesized Cu-PANI nanocomposites shows better crystallinity of synthesized products. The broadening in peaks in XRD pattern indicates that reduced size of nanoparticles. UV-Vis spectroscopic characterization confirms the formation of PANI in doped state and FTIR spectroscopic measurements confirms the interaction of copper nanoparticles with the PANI matrix due to appearance of significant blue shift. The low thermal conductivity of PANI is the main restriction to the applications of it as high dielectric constant material in energy storage devices. To obtain the higher thermal conductivity, in situ method for composites with metal nanoparticles have positives due to better and uniform dispersion in the matrix. Thermal conductivities in the synthesized nanocomposites with different concentrations of filler material are measured including pure PANI matrix in a wide temperature range of zero to 100 °C. The enhancement in thermal conductivity is explained with the help of existing theories for heat transfer in composite materials containing nanoscaled particles.
In this work, we explore the predictive capability of SAFT-γ-Mie [1] to model the phase equilibria of the ternary mixtures. The Statistical Associating Fluid Theory, stemming from the first order perturbation theory of Wertheim [2], was implemented in this work with a group contribution approach and the generalized Mie potential to represent segment-segment interactions. In the resulting SAFT-γ-Mie, complex molecules are represented by fused segments representing the functional groups from which the molecule may be assembled. All interactions, both like and unlike, as implemented in this work were determined from experimental data of systems comprising the constituent groups.

References


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Toluene was the first reference liquid to be proposed (after water), as it is widely used as a basic compound for chemical synthesis and as an organic solvent. Furthermore, its unusually wide temperature range in the liquid phase (178 to 384 K) and its resistance to decomposition, makes it an ideal reference liquid for viscosity calibration purposes and apparatus validation. Thus in 2001, under the auspices of the International Association, a correlation for the viscosity of toluene as a function of temperature and density was proposed by Assael et al.[1]. The temperature range covered was from 213 to 373 K, and the pressure range from atmospheric up to 250 MPa. The standard deviation of the proposed correlation was 2.7% (within a 95% confidence limit). Following the publication of new low-temperature experimental data on the viscosity of liquid toluene along the saturation line, in 2006 a new correlation for the viscosity of toluene along the saturation line was published by Santos et al. [2]. Recommended values were proposed with uncertainties of 0.5% (at the 95% confidence level), for temperatures between 260 K to 370 K, and 2% for 210 K to 260 K and 370 K to 400 K. Furthermore, the value of $554.2 \pm 3.3 \mu Pa s$ was proposed for the viscosity of toluene at 298.15 K. In 2012 an equation of state for toluene was published by Lemmon and Span,[3] thus making possible the development of a wide range viscosity correlation for toluene. Hence, in this work, based on critically-assessed literature data, a new wide-ranging correlation for the viscosity of toluene, valid over gas, liquid, and supercritical states, is proposed.

References

Creating an effective apparatus for universal feedstock is one of the most important problems in the materials development processes, particularly in the petrochemical and chemical industries. In this paper, we present the results of a study of the problem of optimal hardware design for hydrocarbon processing. As an example, we examined the process of oxidative dehydrogenation (ODH) of n-butane to butadiene. Theoretically optimal temperature profile (TOTP) was defined. We applied Pontryagin’s maximum principle, which takes into account the maximum output of desired product. Mathematical model of the kinetics of ODH of n-C4H10 to butadiene was considered. The results show that changes in the initial partial pressure of n-C4H10 in (3-6 kPa) range increase the output of butadiene from 22.4% to 26%. Further increase in the initial partial pressure of n-C4H10 from 6 to 9 kPa decreases the output of the desired product to 23%. At the initial partial pressure of n-C4H10 3 kPa, increase in the initial partial pressure of oxygen (PO2) leads to decrease in the output of butadiene from 25.3% at PO2 = 2 kPa to 22% at PO2 = 7 kPa; and to 16% at PO2 = 12 kPa. Numerical solution of TOTP problem has revealed the existence of optimal region of regime parameters for ODH of hydrocarbons. We found the principal possibility of conducting the process of ODH of n-C4H10 to butadiene in an adiabatic reactor with intermediate heat removal and section-by-section feed.
This paper is focused on the study for the effects of chemical reaction on the steady two-dimensional flow and heat transfer to Sisko nanofluid over a non-linearly stretching sheet with convective boundary condition. Our nanofluid model incorporates the influences of the thermophoresis and Brownian motion. A similarity transformation is used to transform the governing partial differential equations to a system of non-linear ordinary differential equations. The resulting ODEs are successfully solved numerically with the help of fourth order Runge-Kutta method (RK45) with the shooting technique. The effects of various parameters like the power-law index, stretching parameter, the thermophoresis, Brownian motion and chemical reaction parameters on the flow and temperature and concentration profiles are discussed and graphically presented. To see the validity of the present work, we made a comparison with the earlier published results under limiting cases.
Effect of the Condition Parameters in the Synthesis of Mesoporous Zirconia by using Cetyltrimethylammonium Bromide (CTAB) as Template

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Actually, there are several synthesis procedures for the syntesis of zirconia mesopores by using different kind of templates and zirconium oxide sources. For example triblock copolymer non ionic surfactant and zirconium nitrate hydrate. However, they are complex procedures in many cases. Mesoporous zirconia was synthesized using both Sol – Gel and Soft hydrothermal treatment methods. Several runs were carried out in order to determine the effect of the different synthesis conditions such as amount of water and alkaline material, type of alkaline material and aged time. The effects produced were analyzed by x-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. In this study, we demonstrated that for the synthesis of zirconia mesopores is more convenient synthetizing by the following conditions: soft temperature conditions, high molar ratio between alkaline materials and Zr ions, and short aged periods such as 80 °C, NaOH/Zr = 8, and 1 day, respectively. The results showed that the optimal molar ratio of the reagents was ZrOCl2*8H2O:CTAB:NaOH:H2O equal to 1:2:8:75 at 80 °C for one day as the best conditions to form mesoporous zirconia. The objective in this research is to find an easy procedure to the synthesis of mesoporous zirconia by using CTAB as template.
Actually, there are several synthesis procedures for the synthesis of zirconia mesopores by using different kinds of templates and zirconium oxide sources. For example, triblock copolymer non ionic surfactant and zirconium nitrate hydrate. However, they are complex procedures in many cases. Mesoporous zirconia was synthesized using both Sol – Gel and Soft hydrothermal treatment methods. Several runs were carried out in order to determine the effect of the different synthesis conditions such as amount of template and alkaline material, type of alkaline material and aged temperature. The effects produced were analyzed by x-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. In this study, we demonstrated that for the synthesis of zirconia mesopores is more convenient synthesizing with soft temperature conditions, high molar ratio between alkaline materials and Zr ions, and strong alkaline material such as 100 °C, NaOH/Zr = 6, and 100 °C for 1 day, respectively. The results showed that the optimal molar ratio of the reagents was ZrOCl$_2$$\cdot$8H$_2$O:CTAC:NaOH:H$_2$O equal to 1:0.5:6:75 at 100 °C for one day as the best conditions to form
mesoporous zirconia. The objective in this research, is to find an easy procedure to the synthesis of mesoporous zirconia by using CTAC as template.
Low-viscosity ionic liquids (ILs) based on the anions \([\text{C(CN)}_3]^-\) (tricyanomethanide) and \([\text{B(CN)}_4]^−\) (tetracyanoborate) are currently discussed as possible working fluids, e.g., for solar cell applications or gas separation processes. In the present study, the dynamic viscosity of such ILs carrying a homologous series of \([\text{alkyl-MIM}]^+\) (1-alkyl-3-methylimidazolium) cations was investigated via the determination of the translational particle diffusion coefficient by using dynamic light scattering (DLS). For a successful determination of the dynamic viscosity, the long-term stability of silica, melamine resin, and polystyrene particles dispersed in the ILs as well as their particle diameters ranging between 100 and 500 nm were analyzed. For the semi-transparent \([\text{C(CN)}_3]^-\)-based ILs, also the influence of the applied laser power on the measured particle diffusion coefficient was studied. The dynamic viscosity of the four pure ILs forming stable particle dispersions was obtained with an uncertainty of about 5% \((k = 2)\) for temperatures from 283.15 to 353.15 K at atmospheric pressure and agrees well with literature data. Absorption of \(\text{CO}_2\) in the IL at pressures up to about 10 bar induced a distinct decrease in the dynamic viscosity. Differences between the viscosities of the different systems can be explained by varying strength of molecular interactions and structural effects. In a further step, the simultaneous determination of the dynamic viscosity and mutual diffusivity of binary mixtures of ILs with dissolved \(\text{CO}_2\) is proved. Here, scattered light governed by fluctuations in the particle concentration as well as in the molecular composition is analyzed simultaneously.
Measurement of Binary Diffusion Coefficients of CO$_2$ in Several Liquid Alkanes

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Diffusion coefficients of CO$_2$ in hydrocarbons is relevant to many disciplines, with the field of enhanced oil recovery being one contemporary example. Diffusion not only plays a central role in mass transport in porous material at low flow rates but is also one of the determining factors in the rate of absorption of CO$_2$ into the reservoir fluids. However there is a lack of reported measurements in the literature for CO$_2$-hydrocarbon mixtures under relevant (HTHP reservoir) condition. The Taylor dispersion technique has been used to measure diffusion coefficients of CO$_2$ in a homologous series of alkanes over a range of temperatures, (298 – 423) K and pressures from (1 to 69) MPa. Six hydrocarbons, ranging from hexane to hexadecane, were studied as representative model components of a typical reservoir fluid. Measurements were performed using a Taylor dispersion apparatus. The results have an estimated relative uncertainty of 1.5% with a coverage factor of 2. It is found that, in contrast to aqueous systems where there is a negligible effect of pressure on the measured diffusion coefficients, diffusion of CO$_2$ in hydrocarbons is a strong function of pressure, with up to a 45% decrease in values between (1 and 69) MPa at a given temperature. The data have been correlated using a model based on the rough hard sphere theory. This correlation requires knowledge of the molar volume of the solvent at the specific state point and two fitted parameters. The effect of the solvent on the two fitted parameters will be discussed further.
The solubility curves of binary mixture for 2-phenyl butyronitrile(2-PBN) and 3-phenyl propionitrile(3-PPN) in supercritical carbon dioxide are measured by static method at five temperatures (313.2, 333.2, 353.2, 373.2 and 393.2 K) and pressure up to 34.44 MPa. Both carbon dioxide + 2-PBN and carbon dioxide + 3-PPN systems have critical mixture curves that show maximums in pressure-temperature space between the critical temperatures of carbon dioxide and 2-PBN or 3-PPN. The solubility of carbon dioxide for two systems at a constant pressure decreases with the increase of temperature. The carbon dioxide +2-PBN and carbon dioxide +3-PPN systems exhibit type-I phase behavior. The experimental results for the carbon dioxide + 2-PBN and carbon dioxide + 3-PPN binary systems are correlated with Peng-Robinson equation of state using a mixing rule including two adjustable parameters (kij, ηij).
Enhanced understanding of thermal properties of hydrate bearing sediments provides the basis to explore natural gas hydrate both as a promising energy resource and as potential risks to global climate and large-scale seafloor stability. Current database remain limited and few previous studies on methane hydrate bearing sediments have not been able to capture the sequential changes in thermal properties during hydrate formation and dissociation, whereas vigorous phase changes occur in this unsaturated system particularly during gas production. This study reports the thermal conductivity of methane hydrate bearing sediments at various hydrate/water/gas saturations using transient plane source technique (TPS). We propose and validate a simplified model to obtain thermal properties from single-sided TPS signatures. Results reveal that lithological stress controls the thermal properties of water-saturated hydrate bearing sediments; yet gas saturation becomes a dominant role in unsaturated specimens. Although hydrate and water have almost the same conductivity, the increase in thermal conductivity due to hydrate formation remains true in unsaturated sediments as observed in saturated conditions. Differently, the thermal conductivity of unsaturated hydrate bearing sediments has an evident increase when hydrate saturation exceeds ~30%, shifting from the geometric mean model prediction upward to a Pythagorean type model with the fitting parameter $\alpha \approx 0.15$. We also observe thermal conductivity hysteresis in sediments experienced hydrate formation and dissociation, which may have caused water redistribution. During hydrate dissociation, the sediments thermal conductivity temporarily increases when hydrate and water coexist in the pores. These observations imply that the decrease in sediments thermal conductivity during gas production may be larger than expected, particularly when the hydrate saturation drops below ~30% creating a thermal barrier for further hydrate dissociation. These data can also improve current simulators to capture the thermal behavior of hydrate reservoirs during gas production.
Poly(2-hydroxyethyl methacrylate) (PHEMA), a synthetic crosslinked hydrogel, with outstanding ability to absorb and retain a high water content and still maintain their solid state, has been studied as scaffold for methane gas hydrates. The high water content, excellent hydrophilicity and interconnected pores of these hydrogels could be ideal to support the methane hydrate formation and to enhance gas permeation and interactions with water molecules. The heat released during the formation of 1 kg of methane hydrate is as much as 438.54±13.78 kJ. Whether the heat can be removed from the hydrate-hydrogel system in time is critical to the formation of methane gas hydrates. In this work, thermal conductivity is investigated for different temperatures and monomer contents to better understand thermal behaviors of PHEMA hydrogel during the hydrate formation process. Several theoretical models were applied to calculate hydrogel’s thermal conductivity and the prediction results were compared with experimental values. Results were found that thermal conductivity strongly depends on monomer content and ambient temperature. With monomer content ranging from 100 wt% to 5 wt%, thermal conductivity can increase from 0.1259 W/(m·K) to 0.5907 W/(m·K). At some point below 273 K, the thermal conductivity of all hydrogel samples experiences a sudden rise to around 1.5 W/(m·K), about 200% larger. Other thermophysical properties like heat capacity and thermal stability were also investigated using differential scanning calorimetry and thermogravimetric analysis respectively.
Unimodal and bimodal colloidal solutions are extremely useful model systems for the study of nucleation and vitrification. As the packing fraction of a unimodal colloidal solution is increased beyond the melting point, it crystallizes into a solid. But for the bimodal solution, the polydispersity inhibits crystallization and therefore promote a glass transition, where the system undergoes a transition to an amorphous solid [1]. Because of the convenient size and time scales of the colloidal solutions, colloidal crystallization can be studied using light scattering microscopy [2]. One of the main properties measured is the intermediate scattering function (ISF), which is the auto-correlation function of the density-density fluctuations. Molecular Dynamics (MD) simulations of hard-sphere systems [3] have been performed to provide a comparison with experiments, but none have taken into account the hydrodynamic interactions (which are present in real colloidal systems) by simulating the solvent explicitly. We have used MD simulations that simulate the solvent explicitly, to conduct a systematic study of the ISF’s for both unimodal and bimodal colloidal solutions near the melting point and in the metastable region. The aim of this study is to reveal new quantitative information about the differences between the two systems, and the causes of metastability, providing a better understanding of the processes that inhibit crystal formation and promote the glass transition.

References


Thermophysical Properties of Aqueous Solutions of Sodium Naproxen

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Non-Steroidal Anti-inflammatory Drugs (NSAIDS) are used to reduce the fever and to treat pain or inflammation caused by headache, toothache, back pain, arthritis, menstrual cramps or major injury. NSAIDS include sodium salicylate, sodium naproxen, sodium salt of meclofenamic acid and Sodium naproxen. Sodium naproxen reduces the chemical signals in our body that cause pain. Major solvent medium for the biochemical reactions that occur in our body is water. To understand the type and extent of physicochemical interactions between drug and water, thermodynamic, transport and acoustical properties are required. These thermophysical properties of aqueous solutions of sodium ibuprofen, sodium salicylate, and sodium salt of meclofenamic acid have been reported in earlier publications [1-3]. This paper reports density, viscosity, ultrasonic velocity, conductivity, and refractive index data of sodium naproxen water solutions at (298.15, 303.15, 308.15, and 313.15) K. Density and conductivity data of sodium naproxen water solutions reported in the literature have been compared with new generated data. New data of density, viscosity, ultrasonic velocity, refractive, and conductivity are correlated with molality of the solutions. To get the information regarding the nature of sodium naproxen-water interaction, partial molar volume, isentropic compressibility, apparent molar isentropic compressibility, and limiting molar isentropic compressibility of sodium naproxen have been calculated.

References

Acid gases (mainly CO₂ and H₂S) are usually removed from gaseous streams by countercurrent contact with an aqueous amine solution. This is a consolidated industrial technology and is preferred to physical absorption because of the presence of the amine in the liquid phase, which undergoes to chemical reactions and so enhances the mass transfer. Due to the exothermicity of reactions, a temperature increase occurs in the absorber, affecting the equilibrium and the amount of absorbed acid gas, while in the regenerator the energy requirement at the reboiler strongly depends on the heat of desorption. Correct information on the enthalpy, then, is fundamental to design the acid gas removal section of an industrial plant, mainly in an energy saving perspective. The aim of the work is the analysis of the thermodynamics of the system composed of CO₂, water and MethylDiEthanolAmine (MDEA), a tertiary amine widely used also if a separate removal of H₂S and of CO₂ is desired. The study is focused on the computation of the heat of absorption, which, in the open literature, is a field less investigated than the one related to VLE calculations. It is related to the description of the Vapor-Liquid Equilibrium, performed with the Electrolyte-NRTL model, and thus of the adopted VLE parameters. New parameters have been obtained and checked against experimental data of VLE and of heat of absorption. They can be implemented in the commercial software ASPEN Plus® and employed for simulations of the amine scrubbing scheme.
It was shown that in the system TlFeS$_2$ – TlGaS$_2$ the series of solid solutions TlFe$_{1-x}$Ga$_x$S$_2$ (x = 0.01; 0.025; 0.05 and 0.075) is formed. On the basis of radiographs of polycrystalline samples of these solid solutions at room temperature by Rietveld full profile analysis unit cell parameters of these crystals were calculated. It is shown that with increasing concentration of gallium the parameter $a$ decreases, $b$ increases, and parameter $c$ almost remains unchanged. The goal of this report is the investigation of the thermoelectric properties, the temperature-dependent conductivity of TlFe$_{1-x}$Ga$_x$S$_2$ (x = 0.025) solid solution and the establishment of conduction mechanism. Electrical conductivity and thermopower were measured in the temperature range of 80 – 355 K. On the temperature dependence of dark ohmic conductivity of the investigated solid solution an exponential section was observed in the temperature range 180-355 K. The slope of this plot was 0.1 eV. With decreasing temperature, the activation energy of conductivity has not constant slope, i.e. continuously decreased with decreasing temperature up to 80 K. The conductivity of this type when the activation energy decreases monotonically with temperature, provided jumps of charge carriers on states lying near the Fermi level. We estimated the density of localized states ($N_F$) in the TlFe$_{0.975}$Ga$_{0.025}$S$_2$: $N_F = 2.9 \times 10^{19}$ eV$^{-1}$ cm$^{-3}$ and average distance of carriers jumps at low temperatures: $R_{av} = 62$ Å. In the temperature range 80 – 150 K the sign of thermopower was positive, which indicates that TlFe$_{0.975}$Ga$_{0.025}$S$_2$ has p-type conductivity. At T = 150 – 355 K TlFe$_{0.975}$Ga$_{0.025}$S$_2$ has n-type conductivity. The temperature coefficient of activation energy of conductivity has been calculated for studied solid solution from temperature dependence of thermopower ($2.98 \times 10^{-4}$ eV/K).
Test Title

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Why doesn't the cursor show up in this box? *yikes!* This is not good!!!
The critical parameters of liquids are usually investigated for stable substances. However, in most practical applications one deals primarily with thermally unstable mixtures (the temperature of thermal decomposition onset for these substances is lower than the critical one). Because of the obvious experimental difficulties, the properties of these substances are less studied and a search for suitable methods for solving this problem is still in progress. The most reliable results for the critical parameters for thermally unstable pure liquids can be obtained by the method of pulse heating [1]. This method is based on tracking the evolution of the signal of spontaneous boiling-up of a liquid under stepwise pressure increase. This approach, however, becomes less efficient for multicomponent liquids characterized by significantly lower intensities of boiling-up. To overcome this limitation, we have designed new technique within the framework of the method of controlled pulse heating of a wire probe - resistance thermometer that we are developing [2]. The technique is based on the phenomenon of threshold changes in the properties of substance in the course of transition from sub- to supercritical state along the isobar. By selecting the probe heating trajectory and an increment in pressure, we find, at certain pressure value, a (reproducible in temperature and amplitude) signal indicating the entrance into supercritical region, and, as a result, the value of the critical pressure of substance. The corresponding value of critical temperature is calculated with an accuracy of 1%, as in the basic method [1]. The report discusses in detail the technique of measurement, its validation using substances with known critical parameters, and the results for a number of industrial oils used in power and refrigeration applications.

References

Test

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This is a test
Due to the lower symmetry, transport phenomena in liquid crystals are much richer than in isotropic liquids. In axially symmetric nematic liquid crystals, where the molecules are approximately oriented in the same direction in space - the director - but where there is no translational order the heat conductivity has two independent components - parallel and perpendicular to the director - and the viscosity is a fourth rank tensor with seven independent components. Therefore, the heat flow and the shear stress and thereby the irreversible entropy production vary with the orientation of the director relative to a temperature gradient or a velocity gradient. Simulations of liquid crystal model systems consisting of soft ellipsoids have shown that the director tends to align perpendicularly to a temperature gradient. Since the heat conductivity is lower in the perpendicular direction than in the parallel direction this means that the heat flow is minimized. In shear flows at low shear rates in the linear Newtonian regime it has been observed both by theoreticians and by experimentalists that the director assumes an orientation angle that approximately minimizes the shear stress, even though this does not follow from the linear relation between the pressure and the velocity gradient. However, in planar elongational flow, where the system is elongated in one direction and contracted in the perpendicular direction, it follows directly from this linear relation that the director must orient either parallel or perpendicularly to the elongation direction because of mechanical stability and that the irreversible entropy production is either maximal or minimal in these orientations. Simulations have shown that the elongation direction is stable and that the irreversible entropy production is minimal in this orientation. Thus we have three examples where the director of a nematic liquid crystal subject to an external dissipative field assumes an orientation that minimizes the irreversible entropy production.
Enhancement of Thermal Diffusivity in Phase-separated Polyimide Blend Films Containing Needle-Shaped ZnO Particles

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Polyimides (PIs) are a typical super engineering plastics obtained by dehydration reaction of poly(amic acids) (PAAs). PIs have been widely used as alignment layer of liquid crystal displays or flexible printed circuit board due to their excellent heat resistance, mechanical properties and electric insulation. Very recently, enhancement of thermal conductivity is strongly demanded for PI insulating layers associated with speeding up and miniaturization of power-ICs. In this study, thermal diffusivity of phase-separated polyimide (PI) blend films containing needle-shaped ZnO (n-ZnO) nanoparticles was investigated. The PI blend films were prepared by blending n-ZnO and precursors of a sulfur- (SD) and a fluorine-containing PI (TF), followed by curing at 350 °C. Phase-separated structures with vertical double percolation (VDP) morphology was observed by SEM, in which each PI phase was oriented along the out-of-plane direction. In addition, n-ZnO particles were selectively confined in TF phase due to the affinity to fluorine. To investigate the effects of thermal conductivity enhancement of VDP morphology and anisotropic shapes of n-ZnO, thermal diffusivity of the composite films was evaluated by temperature wave analysis (TWA). Comparing with a mono-phase PI with dispersed pyramidal-shaped ZnO (p-ZnO), mono-phase PI containing n-ZnO showed higher thermal diffusivity based on the formation of effective heat conduction paths owing to the improvement of mutual contact probability. In addition, the PI blend films containing n-ZnO demonstrated more enhanced thermal diffusivity than the PI blend films containing p-ZnO. From these results, n-ZnO has higher probability for orienting to the out-of-plane direction due to the confinement of n-ZnO particles in tight space formed in the VDP morphology.
Raman scattering is not only applicable for structural characterization of molecular configuration and conformation in chemistry, but also relevant to physical properties of materials, such as temperature and stress. Thus information about temperature of specimen can be evaluated from intensity, Raman shift and linewidth of Raman signals. This provides the theoretical foundation for characterizing temperature by Raman scattering. In this work, a brand-new time-domain differential Raman (TD Raman) technology is developed to measure the thermal diffusivity of materials. The TD Raman technology uses a variable pulsed laser to heat the specimen and probe the temperature variation based on the principle of Raman thermometry and transient electrothermal (TET) technique. To evaluate this technique, silicon tipless cantilevers are used to conduct the experiment. A silicon tipless cantilever is heated by laser pulses and then Raman scattering spectrum of the specimen is collected. First of all, we develop a physical model to relate the accumulated Raman signal to the instantaneous Raman emission with temperature-dependent intensity, Raman shift, and linewidth. Then we develop a physical model to determine the thermal diffusivity of the cantilever by fitting curves of normalized Intensity and Raman shift against time. Sound agreement is obtained between the measured thermal diffusivity and the reference value. The TD Raman technology provides a very promising noncontact technique to measure the thermal diffusivity of materials without need of the temperature coefficients of Raman signals.
A precise knowledge of thermophysical properties, such as surface tension, viscosity, and density of steels in their liquid state is necessary for the understanding and modelling of their infiltration and gas atomization processes. The measurement of the viscosity of liquid Fe-Cr-Mn-Ni alloys (16 wt% Cr, 7 wt% Mn) as a function of nickel content (≤20 wt% Ni) is a key issue of the current work. A novel vibrating finger viscometer for high temperature measurement in liquid iron base alloys up to 1600°C was constructed. The finger is set in motion using a microcontroller powered field coil. The driven harmonic oscillation of the sine wave is at approximately 26 Hz frequency and 625 ± 1 µm peak-to-peak amplitude. The dynamic viscosity (η) of the liquid specimen is then measured as a product of (viscosity x density)$^{0.5}$ as a function of the relative change of the field coil current for a constant amplitude recording of the immersed vibrating finger into the liquid metal. Dimensionless Reynolds number (Re) is estimated according the Stokes boundary layer between the vibrating finger surface and the liquid steel. The characteristic Reynolds numbers are within the laminar flow condition in the present investigation of liquid steels. The viscosity of Fe-Cr-Mn-Ni alloys is decreasing at high nickel content of approximately 20 wt% Ni. The availability of viscosity data of TRIP/TWIP Fe-Cr-Mn-Ni steel alloys delivers relevant input to model the free fall gas-atomization and the infiltration of open foam ceramics using high manganese steel.
Solar thermal collectors (STC) are especially relevant in solar thermal devices for producing heat from the sun ($T < 150^\circ$C), or producing electricity in concentrated solar power (CSP) plants ($250 < T < 800 \, ^\circ$C). A critical component of solar thermal collectors is the surface that facilitates the conversion of solar radiation into useful heat. These solar absorbing surfaces (SAS) require very high solar absorptivity at visible and near-infrared wavelengths and low emissivity in the mid-infrared spectral region. An effective coating requires an absorptivity over 95% and an emissivity below 5% at working temperature. Previous studies of the SAS emissivity have been done by extrapolating reflectivity values from room temperature to the working one or by measuring the total emissivity with an emissometer below 100 $^\circ$C. These methods do not take into account the emissivity temperature dependence and therefore they might lead to significant errors depending on the actual emissivity temperature behavior. Small differences in emissivity values will affect the coating efficiency and have an important economic impact on the thermosolar electricity production. In this work, spectral emissivity of CERMET-based multilayer stacks at working temperature ($600 \, ^\circ$C) has been studied. Normal spectral emissivity was measured between 2 and 20 microns between 250 and 600 $^\circ$C and afterwards the spectral curves were integrated in order to obtain the total emissivity values. In conclusion, despite small emissivity temperature dependence, notable differences between the values obtained directly at working temperature and those extrapolated are found. Therefore, in order to ensure a proper characterization, it is imperative to measure the emissivity at working temperature.

References

In this paper thermal and mechanical properties (dimension changes, mass changes, bulk density, Young’s modulus and internal damping) of the green ceramic body based on illite and fluidized combustion fly ash during firing are presented. These results are also supplemented by a differential thermal analysis. The investigation is performed in the temperature range from 25 °C to 1100 °C with a heating rate 5 °C/min. The samples are made from illite and a varying amount of fluidized combustion fly ash (from 0 mass% to 40 mass%). The processes occurring in the studied samples during firing are identified. Addition of fly ash acts favorably on the firing shrinkage and bulk density. On the other hand, Young’s modulus generally decreases with increasing amount of fly ash.
Accurate measurements of the density of gas mixtures are essential to improving the equations of state used for natural gas processing. They are also required either to correlate transport properties or as essential information to determine, for example, the viscosity values obtained from a vibrating wire viscometer. Single-phase densities of mixtures of methane + carbon dioxide, methane + butane and methane + heptane at pressures either to 30 MPa or below the lower dew point were measured using a commercial dual sinker magnetic suspension densimeter at temperatures between (293 and 373) K with a relative uncertainty of 0.3 %. To determine densities at pressures above the upper dew point (or bubble point) a custom isochoric apparatus, capable of operating at pressures of up to 140 MPa, was constructed. Densities and bubble points were measured with this apparatus at temperatures between (200 and 320) K and pressures to 35 MPa. The uncertainty in density measured with this apparatus was better than 0.2 %. The measured densities from both apparatus and the bubble points from the isochoric apparatus will be compared with those calculated using the GERG 2008 equation of state and literature data.
Isobutanol (CAS NO: 78-83-1) and n-hexanol (CAS NO: 111-27-3) as a biofuel, which have been got more and more attention due to their high calorific value and combustion performance. The study of these compounds present obvious industrial interest in engineering applications. New density data for isobutanol and n-hexanol over 9 isotherms \((283.15 \leq T \leq 363.15) \text{ K}\) and 16 isobars \((0.1 \leq P \leq 100) \text{ MPa}\) are reported. In this work, the experiment was conducted using a high-pressure vibrating tube densimeter system, which was calibrated with vacuum and water by the method of Lagourette et al. Moreover, R134a has been used as a reference fluid to validate the densimeter. A series of experimental data points have been measured in the framework of this work. The uncertainty of each obtained datum was estimated, and the maximum expanded uncertainty with a level of confidence of 0.95 \((k = 2)\) of density measurement for isobutanol and n-hexanol were 0.04% and 0.03%, respectively. The experimental density data were fitted with the Tait-like equation with an absolute average percentage deviation of 0.019% and 0.034% for isobutanol and n-hexanol, separately. In addition, these data were used to analyze the isothermal compressibility and the isobaric thermal expansivity for these fluids.
Thermophysical Properties of Tetracyanoborate Based Ionic Liquids in Dependence on Temperature at Atmospheric Pressure

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This work represents a continuation of former investigations where dynamic viscosity, interfacial tension, density, and refractive index of ionic liquids (ILs) composed of systematically varied cations and anions were studied. Here, five ILs based on the anion \( \text{[B(CN)]}_4^- \) (tetracyanoborate) and carrying a homologous series of \( \text{[alkyl-MIM]}^+ \) (1-alkyl-3-methylimidazolium) cations \( \text{[EMIM]}^+ \) (ethyl), \( \text{[BMIM]}^+ \) (butyl), \( \text{[HMIM]}^+ \) (hexyl), \( \text{[OMIM]}^+ \) (octyl), and \( \text{[DMIM]}^+ \) (decyl) were investigated by using conventional techniques and surface light scattering (SLS) at atmospheric pressure. For these ILs currently discussed regarding their potential use in solar cell applications or gas separation processes, an Abbe refractometer was used for the measurement of the refractive index in the temperature range from (283.15 to 313.15) K. The density was measured between (283.15 and 363.15) K with a vibrating tube densimeter, while the self-diffusion coefficients of the cation and the anion were obtained from nuclear magnetic resonance (NMR) spectroscopy from (273.15 to 318.15) K. The interfacial tension was measured with the pendant drop technique at room temperature. Based on this datum and the temperature dependence of the density, the interfacial tension for all relevant temperatures was estimated via an appropriate prediction model. For the ILs studied within this work, the ratio of dynamic viscosity to interfacial tension could be directly accessed by SLS in a first order approximation. Combining the results from SLS with those for density and interfacial tension from conventional methods, the dynamic viscosity could be obtained in the temperature range from (283.15 to 363.15) K with an estimated expanded uncertainty \( (k = 2) \) of less than 3\%. All results were compared with literature data and show the influence of the varying alkyl chain length in the cation on the thermophysical properties of \( \text{[B(CN)]}_4^- \)-based ILs.
Ionic liquids (ILs) based on the tetracyanoborate ([B(CN)_4]⁻) anion are potential working fluids for the separation of carbon dioxide (CO₂) from flue gas. For a selective separation of CO₂ from other flue gas components, reliable mutual diffusivity and solubility data are required for mixtures of ILs with dissolved gases. In the present study, dynamic light scattering (DLS) and molecular dynamics (MD) simulations were used for the characterization of the molecular transport in binary mixtures of the IL 1-ethyl-3-methylimidazolium tetracyanoborate ([EMIM][B(CN)_4]) with the dissolved gases CO₂, nitrogen, carbon monoxide, hydrogen, methane, oxygen, and hydrogen sulfide at temperatures from 298.15 to 363.15 K and pressures up to about 60 bar. For the binary mixtures of the IL with gases, the mutual diffusivities measured by DLS can be compared with self-diffusivities of the corresponding gases calculated by MD. At infinite dilution of the dissolved gas, mutual diffusivity and self-diffusion coefficients should match, which was confirmed by our study. Furthermore, experimental mutual diffusivities and simulated self-diffusion coefficients are in good agreement with literature. The results from DLS and MD reveal that for the IL hydrogen mixtures distinctly larger diffusion coefficients are obtained in comparison to mixtures with all other gases. This behavior might be caused by the quantum characteristics of hydrogen and results in the failure of a correlation of the mutual diffusivities with the molar volume of the gas at its normal boiling point.
An evaluation of current state of experimental studies and theoretical calculations of thermodynamic properties of binary mixtures of cyclohexane with n-alkanes has been carried out. The overview has showed that experimental data are scarce and unsystematic. It seems not to have been subjected to overall analysis. The measurements have been carried out only for some types of mixtures and compounds. To determine thermodynamic properties of mixtures the acoustic method has been used. The binary mixtures of cyclohexane with n-octane, cyclohexane with n-dodecane and cyclohexane with n-hexadecane have been chosen as the subject of the study. The speed of sound in the liquid mixtures has been measured using technique of direct determination of transit time of acoustic pulses through known distance. The measurements were made at temperatures from 298 to 433 K and pressures from 0.1 to 100.1 MPa with an inaccuracy not exceeding 0.15%. The experimental speed of sound data have been obtained for the first time. The own speeds of sound obtained at atmospheric and elevated pressures as well as literature values for density and isobaric heat capacity at atmospheric pressure have been used to calculate the different thermodynamic properties over a wide range of parameters. As a result, the values of density, isobaric and isochoric heat capacity, adiabatic and isothermal compressibility, excess molar volume become available. The temperature, pressure and mixture composition dependences of thermodynamic and excess properties have been discussed. Comparison between the obtained values for density and those available in the literature has revealed good agreement.
A novel and reliable ac heating – dc detecting method is developed for active thermoelectric scanning thermal microscopy, which can map out the local thermal property imaging by point heating and point sensing with nanoscale spatial resolution. The thermoelectric probe is electrically heated by an ac current and the corresponding dc thermoelectric voltage is detected. Using the measured dc voltage, the temperature information can be extracted with the known Seebeck coefficient of the thermoelectric probe. The validity and accuracy of this method have been verified by a 25.4 μm K-type thermocouple both by experiment and numerical simulation in high vacuum and in air. The experimental results show that the proposed method is reliable and convenient to monitor the temperature of the junction.
Solubility of the Noble Gases Argon, Krypton, and Xenon in Ionic Liquids

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The primary motivation of the work is to understand the underlying driving force for solubilization of sparingly soluble gases in Ionic Liquids (ILs). Understanding whether the absorption is controlled by enthalpic interactions or entropic interactions can provide insight into ways of controlling the gas solubility in ILs. The solubility of noble gases, including argon, krypton, and xenon were measured in different ILs with varying size and functionality. The ILs investigated include a series of imidazolium-based ILs and a phosphonium-based IL: trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)amide, $[\text{P}_{66614}]\text{[Tf}_2\text{N]}$. The associated Henry’s law constants are reported for all systems, as well as enthalpies and entropies of absorption for systems where multiple isotherms are available. Xenon is the most soluble gas with Henry’s law constants ranging from 10-100 bar while argon is the least soluble gas studied, with the Henry’s law constants on the order of $10^3$ bar. The uncertainties in the measurements of argon, krypton, and xenon solubilities are less than 1%, with lower than 3% deviation in the Henry’s law constants from the associated smoothing curves. The solubility of xenon increases as the temperature decreases, and all three gas solubilities increase as the alkyl chain length on the imidazolium increases, which indicate a strong correlation between the noble gas solubility and the IL molar volume. A general volume dependence of the noble gas solubility in ILs is obtained.
Hi Gary this is a test

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Carbon dioxide (CO$_2$) has an important impact on the climate and is therefore widely studied. Huge efforts are being made, for instance to reduce emissions of CO$_2$ to the atmosphere, by capture- and sequestration techniques. In that context, carbon membrane is a promising and cheap material to capture CO$_2$. Knowledge of heat and mass transport of the gas in a graphitic material is essential to design a new class of material. Boundary driven non-equilibrium molecular dynamics is a reliable technique to obtain thermal conductivity of CO$_2$ in a wide range of temperature and pressure [Trinh et al. J. Chem. Phys. 141, 134504 (2014)]. Recently we found that there are two layers of CO$_2$ adsorbed on a graphite surface [Trinh et al. Chem. Phys. Lett. 612, 214 (2014)]. These layers can be considered as distinct thermodynamic systems and are in equilibrium between each other. In this work, we will discuss the transport of heat and mass of CO$_2$ in a carbon membrane under a temperature gradient parallel to the surface of the pore. By non-equilibrium molecular dynamics simulations, we will show that the pore size and the number of adsorbed layer have an important effect on the transport properties. This will add to the basic understanding of thermal diffusion of CO$_2$ gas in carbon material.
The aim of the present study is the removal of acid gases from the pre-combustion and natural gas sweetening process using physical solvents. In the pre-combustion process, a fuel is gasified to produce syngas, which is a mixture of carbon monoxide (CO) and hydrogen (H₂). However, the syngas also contains several impurities like carbon dioxide (CO₂), nitrogen (N₂) and sulfur compounds (e.g., hydrogen sulfide, H₂S). Similar impurities are also present in raw natural gas. These sour gases should be removed to meet customer and pipeline specifications. CO₂ should be removed to avoid dry ice formation during the liquefaction of the gas and due to the low caloric value of the gas, while H₂S is highly corrosive for the pipelines. The removal of the acid gases is typically performed in an absorber-stripper configuration using either a physical, a chemical solvent or a mixture of both (hybrid) solvents. The choice of the solvent is case specific and depends on many factors like the type and concentration of the impurities, the composition, the temperature, the pressure and ultimately the product specifications. However, chemical solvents (e.g., amines) are most widely used in the natural gas industry. Although amines are very effective in reducing the acid gas concentration, especially at low acid gas partial pressures, it have several serious drawbacks. These include their high energy requirement for solvent regeneration, volatility, corrosivity and the low CO₂/H₂S selectivity. Since the natural gas sweetening and the pre-combustion process operate at high pressures, physical solvents can be applied for acid gas removal and their use are in fact nowadays preferred over the traditional amine solvents. In the past decade, ionic liquids (ILs) have emerged as a promising physical solvent for acid gas removal. ILs are defined as salts with melting point lower than 100 °C and characterized by a very low vapour pressure, high thermal and chemical stability. The solubility data of acid gases are extremely important for the optimal design of absorption columns. However, experimental data of poorly soluble gases (e.g., CH₄, N₂ and H₂) and toxic gases (e.g., CO and H₂S) are scarcely reported in the literature. Moreover, experimental data for the solubility of gas mixtures in solvents, which requires an increased experimental effort, are even more scarce. Here we use Monte Carlo simulations to compute the solubility of the pure gases CO₂, CH₄, CO, N₂, H₂S, H₂, nitrous oxide (N₂O) in several conventional solvents (e.g., Selexol, Purisol, Rectisol and Fluor solvent) and ILs. In addition, solubility of some gas mixtures relevant for the natural gas sweetening and the pre-combustion process has been computed as well. The molecular simulation results are compared with available experimental data [1]. The results show that molecular simulation can be a powerful tool, in the absence of experimental data, to obtain gas solubilities in complex solvents.
Study of the Heater Plate Flatness Affecting the Thermal Conductivity Measurement using Guarded Hot Plate Technique

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Guarded hot plate (GHP) method widely used to the thermal conductivity measurement of insulating materials is introduced and tested at CMI (Czech Metrology Institute) within the project of the European Metrology Research Programme SIB52 Thermo. The material (specimen) is inserted between two heater plates. The temperature difference of a hot and a cold plate as well as the knowledge of the heat flow through the specimen and a thickness of the specimen enable to calculate the value of the specimen thermal conductivity according to Fourier’s law. However, several problems have to be solved to ensure the heat flow through the specimen is unidirectional and perpendicular to the heater plates. As the title of GHP suggests, the central part of hot plate with desired temperature and input heater power is surrounded by the guard plate to protect unidirectional flow in the central part of specimen. As regards the measurement of thermal conductivity of solid materials, one of the important design requirements for the GHP apparatus is a sufficient flatness of heater plates. The deviations from the plane cause insufficient contact with the specimen leading to the disruption of desired unidirectional heat flow. Therefore, the temperature profile of the specimen has to be calculated under different conditions of the plate flatness. With respect to the temperature range within the GHP can operate (up to 800°C) the calculation is provided also with the contribution of the radiation which becomes more significant with the increasing temperature. Above 300°C the combined model consisted of the conduction and the radiation part has to be taken into account. The output of this work is the mathematical model considering the aspects which can contribute to the inhomogeneity of the specimen temperature profile and the comparison with the experimental results.
Phase Behavior of Liquid and Gaseous Fluids in Lyophilic and Lyophobic Porous Media

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The results of calorimetric investigations of phase behavior of liquid and gaseous hydrocarbons in lyophilic (wettable) and lyophobic (non-wettable) porous media are presented. Quartz powders are used as lyophilic porous media for hydrocarbons. Lyophilic properties of quartz powders are manifested through increased capillary condensation as well as sorption of hydrocarbons. As a result the phase diagrams of hydrocarbons in lyophilic porous media are transformed in compare with bulk diagrams. Quartz powders covered with water film are used as lyophobic porous media for hydrocarbons. Quartz powders covered with thin water film are lyophilic or lyophobic depends on the length of n-alkane's molecule (with increasing of hydrocarbon chain the lyophobic properties of water film are increasing). Ethane wets water surface completely. Propane and i-butane wet the water surface partially (mostly non-wetting). Due to the lyophobic surface of water the capillary effect for evaporation of liquid hydrocarbons is take place. Evaporation of liquid hydrocarbon (propane, for example) occurs at pressure above the saturation vapor pressure of this hydrocarbon in bulk due to a curvature and non-wettability of water surface. The result of this effect is a shift of the vapor - liquid equilibrium line of hydrocarbon in the quartz powder covered with water film in compare with the bulk equilibrium line. Transformation of hydrocarbon phase behavior affects on the gas hydrate transition that is manifested through the hydrate upper quadruple point shift into the higher temperature and pressure. The result of this shift is expansion of the gas hydrate stability field and possibility of existence of the state of “superheated” gas hydrates.
For the first time using a new type of combined volumetric equation of state we carried out a unified description of thermal and caloric properties of one-component fluids. The efficiency of our method is tested on CO2 and SF6. The coefficients of the combined equations were found in the approximation p,V,T - data up to 30 MPa. The calculation heat capacity Cv performed in a wide range of parameters of single-phase state, including the critical region. As a result, we obtain a description p,V,T - the data in the single-phase region of the gas and liquid states from the triple point up to supercritical temperatures with an error at a pressure of ~ 0.6%. The curves of the specific heat Cv, calculated on the same isochores and isotherms, in which are available experimental data on Cv, show a good agreement with the experimental data within ± 8% in different areas of the state including the critical region. Thus, the proposed method allows us using only P, V, T-data of one-component liquids to predict the behavior of their caloric properties.
New trends in the publication of thermophysical properties data for chemical substances are reviewed using, as an example, the properties of water and steam – the principal heat carriers and working bodies in thermal and nuclear power industries. The advantages and disadvantages of traditional publication on paper are examined in comparison with the modern electronic delivery via Internet. One important requirement for the latter is the inclusion of interactive calculations. Additional requirements for online calculation tools may include low or no cost to the users, multiple platforms (Windows, Android, Linux etc.), multilingual interface (English, Russian, Chinese, German, Spanish, etc.), traditional math operators and functions, 2D and 3D graphic capabilities, animation, numerical and symbolic math, tools for solving equation systems (algebraic, differential, etc.), derivatives, integrals, as well as programming tools for setting conditions, local functions, etc. Using of computer animation for verification of functions for calculating thermophysical properties of substances is reviewed. An analysis of relevant Internet resources is given. Certain aspects of the work of the International Association for the Properties of Water and Steam (IAPWS) are described. New information technologies are described for publishing the data on thermophysical properties of substances using IAPWS formulations that can trace the errors in the code and optimize calculation process. Specific examples are provided of the development of modern IT resources for the modeling of the properties of chemical substances, including handbooks, desktop calculation software, downloadable online calculations, and calculations that use server technologies such as Mathcad Calculation Server (see the site of National Research University “Moscow Power Engineering Institute”) and SMath (see the site of Knovel, an Elsevier company).
Electronic database directory "Thermodynamic properties of individual substances", created in the ICT Academy of Sciences Soviet researchers since the 50s of this century, at the dawn of the Soviet space program. Handbook published in 4 volumes. Each volume of the handbook "TSIV" consisted of two parts: text (with references) and a table. Subsequent studies were conducted from 1985 to 2004. in the department of chemical thermodynamics High Temperatures of the Russian Academy of Sciences. Directory and its database contains information on more than 2,000 different substances and their compounds. For each substance, available information on its isobaric heat capacity, reduced Gibbs energy, enthalpy and entropy as a function of temperature. The database is designed as a "live" calculations in Mathcad and is available in the public domain on the Internet, except for code calculations. This fact allows us to refer to the function by using Mathcad in other calculations. Researcher, engineer or student can enter the temperature (within the workspace functions) and obtain the value of the four thermodynamic properties. Also shows a plot of these functions, which the user can trace the behavior of the entire temperature range. Each calculation sheet and attached to the table from the directory. Calculations are built using mathematical modeling of polynomial dependencies. The database is complemented by similar calculations in Mathcad 15, Mathcad Prime 3, SMath and Excel. In Excel formulas on the properties of individual substances are presented in a tabular format that makes it easy to transfer their problems in programming languages BASIC, C, Pascal, Java, VBA and others.

Address resource http://twt.mpei.ac.ru/ochkov/VPU_Book_New/mas/index.html
Computer simulation of heat and mass transfer or energy conversion needs special software which enables to calculate thermophysical properties of working fluids. Such software should be installed on a computer and needs to be updated periodically. It is mainly due to the fact that new working fluids and formulations emerge. In addition, errors and inaccuracies in existing computer programs take place, their application domains are extended, and their performance is improved. Such programs are also continuously updated due to changes made in the hardware and operating system software. Users of computer programs on properties of working fluids frequently fail to notice these changes and work with outdated versions. Also, users face additional difficulties if they change their computer and/or operating system: old computer programs cannot be installed and started any longer. Besides most such programs have quite narrow possibilities of their further application in computer simulation. Moreover, it is not possible and/or unreasonable to save in one program or one computer data about all existing working substances. In view of what is said above, and taking into account that at present almost all computers have constant high-speed connection to the Internet, a new technology for "cloud" functions on properties of working fluids is proposed. The technology has been successfully tested on the Internet server located at www.vpu.ru/mas. The calculation server proposes three options of using "cloud" functions: on-line calculations, download and reference. Online resources give a possibility to do "cloud" calculations of thermophysical properties in an interactive mode in accordance with input data of a user. The procedure of downloading enables to download such functions on personal computers. The reference procedure gives a possibility to do Internet reference to the functions on properties of working fluids for developing further calculations in processes of heat and mass transfer or energy conversion.
Diffusion and Soret Effect in Ternary Mixtures

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In mixtures, subjected to a temperature gradient at a constant pressure, the diffusive transport is caused not only by gradients of concentrations but also by gradients of temperature. The mass flow induced by a temperature gradient in mixtures is referred to as the Soret effect (thermodiffusion or thermal diffusion). Nowadays, the Soret effect of almost any binary fluid can successfully be studied under laboratory conditions. The investigation of ternary liquid mixtures is significantly more complex than the binary case and has made progress only during recent years. While binary mixtures are fully characterized by one diffusion and one thermodiffusion coefficient, there are six independent parameters in the ternary case: four diffusion coefficients and two thermodiffusion coefficients. The necessity of resolving two independent concentrations requires two different and independent diagnostics. For this purpose, traditional optical techniques with two laser diodes emitting different wavelengths may provide six independent coefficients. The first experiments have shown that in addition to the experimental difficulties, there are mathematical problems of coefficients extraction from the measured signals. One of the most serious limitations is a property of matrix of the so-called optical contrast factors; i.e; the matrix with elements composed by the derivatives of refractive indices with respect to concentrations. The matrix can be ill-conditioned, and the error in the retrieved concentrations becomes dramatic, preventing accurate measurements. Another problem is resolving of the diffusion matrix. Its seems that only eigen values of the diffusion matrix can be retrieved accurately from thermodiffusion experiment but not the elements.
Surface Tension of Supercooled Water Down to -21°C Measured within a Horizontal Capillary Tube

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New data for the surface tension of metastable supercooled water, i.e., the liquid water at temperatures below the equilibrium freezing temperatures, is presented in this study. A new experimental apparatus based on the measuring technique developed by Ferguson and Kennedy [1] was recently designed and tested [2]. A short liquid thread with a length of 2-3 cm was located in a horizontal capillary tube with inner diameter around 0.3 mm. One end of the capillary tube was connected to the pressure setup with inert gas, while the other end was left open to ambient. The open end of the capillary tube was observed with an optical setup consisting of a laser source, optical prism, lens, and a digital camera. A pre-set overpressure of inert gas in order of hundreds of Pa applied to the closed end of the capillary tube gradually changed the liquid meniscus at the open end from concave to planar and subsequently to convex. The surface tension at the inner liquid meniscus was determined from the overpressure of inert gas corresponding to the flattened outer meniscus. The surface tension of supercooled water was successfully measured down to -21°C. The new data obtained from the horizontal technique agrees well with our previous measurements performed with the modified capillary rise method [3]. The data can be well reproduced with the IAPWS correlation for the surface tension of ordinary water [4] extrapolated below 0.01°C.

References

Isothermal Vapor-Liquid Equilibrium of R161+DMETrEG within the Temperature Range of (293.15-353.15) K

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For the sake of environment, new alternative refrigerants have been looked for in recent years. Ethyl Fluoride (R161) is one of the most promising alternatives because of its high cooling capacity, relatively high volume cooling capacity, and excellent energy efficiency ratio. In addition, it is environmentally friendly because it does not have the ozone depression potential (ODP=0), which means it does no harm to the ozone layer, and has a low global warming potential (GWP=12). For R161 has excellent environmental and thermodynamic properties without corrosivity and toxicity, it was put forward in the absorption refrigeration combined with the corresponding absorbents. To make the refrigerant better applied in the absorption refrigeration system, the suitable absorbent should be selected for matching the R161. Vapor-liquid equilibrium data is the basis and the key of the chemical engineering simulation as well as the refrigerating cycle calculation, and its accuracy directly affects the efficiency and scale of the chemical and refrigeration equipment. On the basis of these, the vapor-liquid equilibrium data of the mixture (fluoroethane (R161) + dimethylether triethylene glycol (DMETrEG)) were obtained from 293.15 K to 353.15 K by a dual recirculation technique. The experimental apparatus set up for vapor-liquid equilibrium was consisted of a high accuracy thermostated bath, a equilibrium cell with sight glasses, a high accurate temperature measure system (the standard temperature uncertainty is less than 10mK), a high accurate pressure measure system (the standard pressure uncertainty is within 1.4 kPa), and a composition measure system (the standard composition uncertainty is within 0.003 mole fraction). The vapor-liquid equilibrium data were correlated by PR equation of state combined with the MHV1 mixing rule and NRTL model. The data showed that there was negative deviation compared to Raoult's law in the mixture (R161 + DMETrEG). Meanwhile, the results obtained in this work were compared with those of the mixture (fluoroethane (R161) + dimethylether diethylene glycol (DMEDEG)).
Microcalorimetric Measurement of a Physical-Chemical Absorbent for CO₂ Capture

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The traditional CO₂ capture material, aqueous monoethanolamine (MEA), have a good CO₂ solubility and a high absorption rate, but is expensive to regenerate in terms of energy cost and solvent loss. Instead of water, an aprotic polar solvent, diglyme, was used to dissolve MEA to form a physical-chemical absorbent MEA+diglyme in this work. To evaluate the performance of proposed absorbent, an experimental apparatus was designed and built up, which combined the microcalorimetry and the isothermal synthesis method. The apparatus was able to measure the CO₂ solubility and absorption heat simultaneously. The calorimeter BT2.15, produced by SETARAM Instrumentation (Caluire, France), was used to measure the heat of CO₂ absorbed by MEA+diglyme pre-stored in the vessel of calorimeter. The isothermal synthesis method has been used to measure solubilities of many vapor-liquid systems including CO₂ in organic solvents, polymers, and ionic liquids. In this work, the isothermal synthesis method was used to measure the load of CO₂ in absorbent corresponding to the absorption heat detected by the calorimeter. The CO₂ solubility and heat of absorption in aqueous MEA were measured to validate the apparatus. Deviations between experimental data and data in literature were calculated, and the calculation indicated a good reliability of the apparatus. Then the CO₂ solubility and heat of absorption in MEA+diglyme were measured. The obtained data were compared with that of aqueous MEA. Results indicated that both CO₂ solubility and absorption heat in MEA+diglyme were less than those in aqueous MEA under CO₂ pressures below ~1200 kPa and MEA concentration of 30 % (mass fraction).
It is well appreciated that placing a fluid under confinement drastically alters both its static and dynamic properties relative to a bulk, unconfined fluid. However, predicting these changes (even semi-quantitatively) remains a scientific challenge, and thus, there exist fundamental knowledge gaps in a number of areas where confined fluids play a central role. Examples include lubrication, friction, and adsorption. In an effort to understand the impact of confinement on fluid properties, recent work has demonstrated that there exists a robust relationship between static fluid properties, such as excess entropy and insertion probabilities, and dynamic fluid properties, in particular, the self-diffusion coefficient, that is independent of the geometry of the system when the confinement is straightforward. However, such relationships have not been observed for confined fluids, which are prevalent in applications such as adsorption. Using Monte Carlo and Molecular Dynamics simulations in tandem, we perform this combined static-dynamic analysis to models of light gas adsorption in simple confinements such as graphitic carbon materials to systematically investigate the effect of the fluid-material interaction strength on the correlation of static and dynamic properties. We observe that fluids confined in strongly attractive pores display three distinct diffusive regimes when cooled below the critical point. These regimes are directly related to the structural arrangement in the pore, and hence, to the thermodynamic properties of the fluid. Even though weaker adsorbing pores exhibit a qualitatively different adsorption isotherm (e.g., the absence of multilayer adsorption), the relationship between the diffusive regimes and the underlying fluid structure is identical to that in strongly adsorbing pores. We perform additional analyses that allow for separation of the average dynamic properties into position-dependent dynamic properties through which we demonstrate how the three distinct diffusive regimes in adsorption processes are related to specific equilibrium structures at the relevant state points.
Thin metal films are widely used as interconnecting wires and coatings in electronic devices and optical components. Reliable thermophysical properties of the films are required from the viewpoint of thermal management. The cross-plane thermal transport and phonon attenuation of two polycrystalline platinum nanofilms with different thickness deposited on glass substrates has been studied by applying the picosecond laser transient thermoreflectance technique. The measurement is performed by applying both front pump-front probe and rear pump-front probe configurations with high quality signal. The determined cross-plane thermal diffusivity of the Pt films greatly decreases compared to the corresponding bulk value, exhibiting significant size effect. The main mechanism responsible for the thermal diffusivity decrease of the present polycrystalline Pt nanofilms is the grain-boundary scattering on the free electrons.
Density and Speed of Sound Measurements of Nonane and Toluene with Dissolved CO₂ at HTHP Conditions

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Thermophysical properties of binary mixtures of hydrocarbons with carbon dioxide have not been studied extensively in the literature, especially at high-temperature and high-pressure (HTHP) conditions. In this work, we have measured the density and speed of sound of the binary systems \([x \text{CO}_2 + (1 - x)\text{C}_9\text{H}_{20}]\) and \([x \text{CO}_2 + (1 - x)\text{C}_7\text{H}_8]\) under HTHP conditions. The mole fractions of CO₂ in the binary mixtures studied were: \(x = 0, 0.2, 0.4, 0.6\) and \(0.8\).

The density measurements were performed at temperatures between \((283\) and \(473\) \(K\)) and at pressures up to \(68\) MPa. The density measurements were carried out with an Anton Paar vibrating-tube densimeter, calibrated with helium and deionised water over the full ranges of pressures and temperatures investigated. The calculated expanded relative uncertainty of density at 95 % probability was found to vary between \((0.09\) and \(0.12\) \%) upon temperature. The results have been correlated with a modified Tait equation and also compared with the predictions of the GERG-2008 equation of state. The speed of sound was studied in the temperature range \((253\) to \(473\) \(K\)) and pressures up to \(400\) MPa by means of a double-path pulse-echo apparatus operating at \(5\) MHz. The ultrasonic cell was calibrated with pure water at \(T = 298\) K and \(p = 1\) MPa against the speed of sound given by the 1995 equation-of-state formulation of the International Association for the Properties of Water and Steam (IAPWS-95) which for that state point, has an uncertainty of \(0.005\%\). Combined with isobaric heat capacity data, density data were extrapolated for pressures up to \(400\) MPa by integration of speed of sound data. Other observable thermophysical properties such as thermal expansion coefficient and compressibility were derived from the measured sound speed data over the full pressure range.
Density Measurements on 0.95 CO₂ + 0.05 CH₄ at the Vicinity of the Critical Point in the Supercritical State by Single Sinker Densimeter

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Measurements of volumetric properties of binary mixture 0.95 CO₂ + 0.05 CH₄ were performed at 300.15 – 313.15 K and 8.0 – 10.0 MPa, which is at the vicinity of the critical point in the supercritical state, with intervals 1.0 K and 0.2 MPa for temperature and pressure, respectively, by single sinker densimeter. The extended uncertainties (k=2) of measurement are estimated to be 21.5 mK for temperature, 3.39 kPa for pressure, and 0.022%ρ for density. The uncertainty contribution from molar fraction to density is possibly up to 0.15%, with mixture preparation and gas absorption and desorption effect as the domination factors. The measurement results were compared with GERG-2004 equation of state. Generally, the deviation from experiment data to GERG-2004 EOS increases when approaching to the critical point, peaking at -4.8% at (301.07K, 7.97 MPa). In an isothermal state with increasing pressure, the deviation reaches maximum when crossing the Widom Line. The isobaric expansibility αₚ, i.e. (∂V/∂T)ₚ, was calculated from the experiment results and a maximal locus of αₚ in the measuring range is obviously observed. The maximal locus stretches close to critical point but the critical point is not on the extension of this maximal locus. This phenomenon is different with that in purity, for which critical point is on the extension of the maximal locus of αₚ.
Speed of Sound Measurements of 2-Ethoxy-2-Methylpropane and 2-Methoxy-2-Methylbutane by Spontaneous Brillouin Light Scattering (BLS)

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Oxygenated compounds are increasingly added to gasoline to increase their octane number. It can also improve engine efficiencies and decrease NOx, carbon monoxide and unburned hydrocarbons emission. Commonly used oxygenates include aliphatic alcohols and methyl ethers. 2-ethoxy-2-methylpropane (ETBE) and 2-methoxy-2-methylbutane (TAME) have been considered as the potential fuel additives as the replacement of 2-Methoxy-2-methylpropane (MTBE), so the knowledge of their thermophysical properties is very important. Speed of sound is one important acoustic property. It affects directly the fuel injection characteristics and the amount of NOx emissions. Speed of sound also permits the estimation of other thermodynamic properties like isentropic and isothermal compressibility, isobaric thermal expansion coefficient, thermal pressure coefficient and the reduced bulk modulus. The speed of sound of ETBE and TAME were measured by employing a spontaneous Brillouin light scattering (BLS) technique. The standard experimental uncertainties in temperature and pressure are 0.016 K, 0.015MPa for \( p < 5.5 \) MPa and 0.03MPa for \( p > 5.5 \) Mpa, respectively. The relative expanded uncertainty in speed of sound was estimated to be less than 0.5% over the whole investigated thermodynamic range. The coverage factor of \( k \) was taken to be 2. The sound speed of saturated n-pentane was measured to verify the experimental system. The experimental results agree well with the sound speed calculated from the multi-parameters EOS proposed by R. Span and W. Wagner(2003). So the speed of sound of ETBE and TAME (mass fraction quoted from Aladdin, > 0.990, GC) were measured at temperatures ranging from 298.15 to 773.15 K and pressure up to 8.5 MPa, including saturated liquid/vapor, compressed liquid and supercritical region. More than 400 new experimental data on the speed of sound of ETBE and TAME were provided. The polynomial representations for sound speed were proposed by employing the experimental results.
Interfacial Tensions of (CO₂ + H₂O + N₂ or Ar or H₂) at Temperatures of (298 to 473) K and Pressures up to 50 MPa

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Interfacial tension measurements of the (CO₂ + H₂O + N₂ / Ar / H₂) and (N₂ / Ar / H₂ + H₂O) systems are reported at pressures of (2 to 50) MPa, and temperatures of (298.15 to 473.15) K. The pendant drop method of imaging a fluid-saturated pendant water drop, surrounded by a water-saturated fluid phase in a high-pressure view cell, is used. In this method, it is necessary to know the density difference between the two phases. To permit calculation of this difference, the compositions of the coexisting phases are first computed from a combination of the Peng-Robinson equation of state (applied to the non-aqueous phase) and the NRTL model (applied to the aqueous phase). Densities of the non-aqueous phase are computed from the GERG-2008 equation of state, while those of the aqueous phase are calculated knowing the partial molar volumes of the solutes. The expanded uncertainties at 95 % confidence are 0.05 K for temperature, 0.07 MPa for pressure. The interfacial tensions in all systems are found to decrease with both increasing pressure and increasing temperature. Empirical correlations are developed for the interfacial tension of the (N₂ / Ar / H₂ + H₂O) systems in the full range of conditions investigated, and these are used to facilitate a comparison with literature values. Estimates of the interfacial tension for the ternary systems, by means of empirical combining rules based on the coexisting phase compositions and the interfacial tensions of the binary sub-systems, are found to be somewhat inadequate at low temperatures.

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Laser Flash Raman Spectroscopy Method for Thermophysical Characterization of Nanomaterials

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Recently, a noncontact technique based on the temperature dependent Raman band shift has been applied for thermophysical characterization of low dimensional nanomaterials. However, in most measurements the laser absorptivity requires to be determined beforehand and the difficulty of accurately determining the laser absorptivity significantly limits the accuracy of this Raman technique. In general, to avoid the direct measurement of the laser absorptivity, a direct current is supplied to eliminate the laser absorptivity in theory, making the experiment more difficult and samples at a risk of burnout. To solve these problems, in this work, a transient “laser flash Raman spectroscopy” method is presented to characterize the thermal properties of low dimensional nanomaterials, with which the laser absorptivity can be easily eliminated and the electricity is needless. The measuring method for the thermal diffusivity and thermal conductivity of individual micro/nano wires is first presented. In this method, a focused short pulsed laser and a continuous-wave (CW) laser in a Raman spectroscopy system are served as a local heater, Raman signal excitation source and also a temperature sensor. Transient and steady-state heat conduction models are established to obtain two independent equations for the thermal diffusivity and laser absorptivity. This new method has been verified by comparing experimental results of a graphite carbon fiber with measurements employing the 3ω method. Further, the method is used to measure the temperature dependent thermal diffusivity and thermal conductivity of individual carbon nanotubes (CNTs), which fit well with theoretical trends. The present transient method has further been extended to 2D nanomaterials. By using a transient heat conduction model in cylindrical coordinate, the thermophysical properties can be determined by fitting the curves of the normalized temperature rise versus the laser pulse width for various laser spot radii. The uncertainty caused by temperature measurement is analyzed theoretically and through a case analysis of silicon nanofilm, changing laser spot radii is proved to be more easily in practical use than changing laser pulse width.
Measurements of $P\rho T$ Properties, Vapor Pressures, Saturated Densities, and Critical Parameters for R 1243zf

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Measurements of $P\rho T$ (pressure - density - temperature) properties and vapor pressures for new low GWP refrigerant R1243zf (3,3,3-trifluoroprop-1-ene; CF$_3$CH=CH$_2$) were made by the isochoric method. Pressure measurements were made with the digital quartz pressure transducer and their uncertainty was estimated to be within 2 kPa. Temperature was measured with 25 Ω standard platinum resistance thermometer and AC thermometer bridge. The uncertainty of temperature measurement was estimated to be within 10 mK. The density was calculated from the sample mass and inner volume of pressure vessel. Nineteen vapor-pressure data and 133 $P\rho T$ property data for R1243zf were obtained in the temperature range from 310 K to 430 K, and pressure up to 6.9 MPa with individual seven runs. On the basis of these vapor-pressure measurements, the correlation of vapor pressures was also proposed. Saturated liquid and vapor densities were directly determined by the visual observation of meniscus disappearance. Fourteen data were obtained in the temperatures from 360.727 K to the critical temperature and in the density range between 182.7 kg/m$^3$ and 723.7 kg/m$^3$. The critical temperature $T_c = 376.93$ K and critical density $r_c = 414$ kg/m$^3$ were determined taking into consideration the meniscus disappearing level and the intensity of the critical opalescence. The critical pressure $P_c = 3517$ kPa was also determined from the vapor pressure correlation made in this work.
Disordered metallic alloys are modeled as a randomly close-packed distribution of nanocrystallites intermixed with randomly positioned atoms. The crystallite size distribution function is measured in a simulated macroscopic medium in two dimensions. In the system of binary alloys, the distribution function is found to be a stationary random property of the medium for given alloy composition. The degree of crystallinity, which is defined as the probability that a particle in the medium is a member of crystallites, is also determined by the composition. The volume of the macroscopic alloy specimen is then fully defined by the statistical measures. When heated, the nanocrystallites within the specimen become smaller in size as a result of increasing thermal fluctuation. We have modeled this phenomenon as a case of thermal dissociation by means of the law of mass action. The crystallite size distribution function is computed for AuCu₃ as a function of temperature by solving some 12000 simultaneous algebraic equations for the degrees of dissociation according to the size distribution of nanocrystallites. The nanocrystallite size distribution function in 3-D is found by transforming the 2-D distribution for this purpose. Linear expansion of the specimen has three contributions: the respective expansions of the crystallites and glassy matter and the temperature dependence of the degree of crystallinity.
Trans-1,3,3,3-tetrafluoropropene (R1234ze(E)) is a new synthetic working fluid with zero ozone depletion potential (ODP) and low global warming potential (GWP), which was screened out as a promising alternative working fluid for refrigeration systems. Comparing with the single component, its mixtures have better adaptability. This study provides fundamental data on the transport properties of this refrigerant mixture in order to evaluate the feasibility of using the mixture in refrigeration systems. Thermal conductivity data for a binary system of {1,1-difluoroethane (R152a, CAS NO. 75-37-6) + trans-1,3,3,3-tetrafluoropropene (R1234ze(E), CAS NO. 1645-83-6)} were measured between (283 and 363) K in the pressure range up to 20 Mpa with 1,1-difluoroethane mass fractions of 0.10, 0.30, 0.50, 0.70 and 0.90, respectively. The experiment was conducted using the transient hot-wire method with single oxidized tantalum hot wire. The performance of the apparatus was tested by measuring the thermal conductivity of saturated liquid toluene from (283 to 363) K, which agreed with recommended values with a maximum deviation of 0.71%. The expanded uncertainty of the thermal conductivity data was less than ±2.0% with the coverage factor \( k = 2 \). The experimental data of the mixtures were correlated as functions of temperature, pressure, and mass fraction, respectively.
Saturated Phase Density Measurements of CO$_2$ + Toluene and CO$_2$ + n-heptane systems at Temperatures from (300 to 450) K and Pressures up to 20 MPa

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The understanding of the density for CO$_2$ + hydrocarbons systems at reservoir conditions is very important for the correct design and the optimisation of carbon storage and enhanced oil recovery processes. While the densities of such mixtures have been reported in single-phase regions, data for the saturated phase density are very limited, especially at the reservoir condition. In this work, new saturated phase density measurements of (CO$_2$ + toluene) and (CO$_2$ + n-heptane) systems have been made at temperatures from 300 to 450 K and pressures up to 20 MPa, with an estimated relative uncertainty of 0.1 %. The measurements have been carried out in an apparatus consisting of an equilibrium cell connected to two high-pressure vibrating-tube densimeters and two syringe pumps. Both densimeters were calibrated with pure water and vacuum over the ranges of pressure and temperature. The results of the measurements are compared with the unsaturated densities of (CO$_2$ + toluene) and (CO$_2$ + heptane) at the same temperatures and pressures as well as data existing in the literature for similar systems. Finally, the new density data are compared with predictions made using theoretical and empirical models appropriate to the particular mixture.
Static Phonon Scattering in Graphene Foam: Uncovered by Residual Thermal Diffusivity at 0 K Limit

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Due to its intriguing thermal and electrical properties, graphene has been widely studied for potential applications in electrodes, conductors, sensor, and energy devices. However, the reported value for its thermal conductivity varies from dozens to thousands of W/mK due to the different levels of alternations and defects in graphene samples. In this work, the thermal transport in suspended four-layer graphene foam (GF) was experimentally studied and reported from room temperature to temperature as low as 10 K. By measuring GF at different lengths, the real thermal diffusivity ($\alpha$) without radiation effect was obtained. The thermal diffusivity of GF shows a linearly increasing behavior with decreasing temperature in the temperature range of 295 to 95 K. At low temperatures it tends to be stable with a slight decrease. By using classical model for thermal conductivity and fitting $1/\alpha$- $T$ curve to the point of $T=0$, we are able to identify the effect of defects scattering and evaluate the static phonon scattering of GF. The ideal thermal diffusivity of GF without effect of defects was subsequently reported. Without measuring the porosity of GF, the intrinsic thermal diffusivity of free-standing four-layer graphene ($\alpha_G$) at different temperatures was obtained based on Schuetz’s model. The ideal thermal conductivity of graphene ($k_G$) against temperature ($T$) profile was calculated. A peak value of 2220 W/mK at 75 K is observed for the thermal conductivity. These results provide an important insight to the thermal transport physics in graphene.
Gas hydrates are crystalline solids that can form and plug subsea oil and gas pipelines. With focus shifting from the complete prevention of hydrate to limiting the severity of hydrate formation, high-performance surfactants (i.e. anti-agglomerants) can be central to the strategy of preventing the formation of a hydrate plug. Currently, the performance of each anti-agglomerant and petroleum fluid pairing is validated qualitatively in a rocking cell, which does not capture the amount of surfactant required for adsorption at the hydrate-oil interface. In this study, a differential scanning calorimeter (DSC) method was developed to investigate methane hydrate formed at high pressure from a water-in-crude oil emulsion. A metastable crude oil emulsion was chosen for this study, for which the droplet size distribution was determined with low-field NMR and visual microscopy. Representative surfactants were added to the crude oil phase across a wide range of concentrations, including model chemicals for an industrial corrosion inhibitor and hydrate anti-agglomerant. The minimum concentrations of these surfactants required for adsorption were successfully identified using repeated hydrate formation and dissociation trials in the DSC, and compared to previously-reported estimates for hydrate systems. The results indicate that corrosion inhibitor chemistries are clearly active at the hydrate-oil interface and were able to stabilize the hydrate dispersion at concentrations above 0.001 wt% in oil. Without the addition of synthetic surfactants, increasing the brine salinity to 10 wt% fully stabilized the hydrate-in-oil dispersion without significantly affecting the water droplet emulsion stability. This suggests that brine salinity is a key parameter in tuning the performance of surfactants for hydrate-in-oil dispersions.
Electrocaloric Relaxor Ferroelectric Polymer Materials for Dielectric Refrigeration: Novel Developments and Future Perspectives

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Electrocaloric effect (ECE) has been known for many decades, however, the relatively small ECE observed
Nowadays more and more network thermal imaging cameras are working over distributed networks, offering the capability of online remote intelligent video surveillance. In this paper, we propose an original intrusion detection and cooperative tracking approach applied for PTZ (Pan/Tilt/Zoom) network thermal imagers. The key module in the proposed approach is real-time FOV (Field-of-View) matching. It is realized in a parallel way. One thread tracks the keypoints employing our ultra-low-weight keypoint description and hybrid SP-Tree, and the other thread handles the three-dimensional mapping task. In the intrusion detection module, after eliminating the offset between current frame and prior frame through FOV matching, it handles the intrusion detection by motion detection in the pre-set surveillance zone. In the cooperative tracking module, it shifts the priority of tracking by imager pose estimation, which is also based on FOV matching, avoiding transferring the local features from one imager to another. Experiments are conducted to demonstrate that the proposed approach is of high accuracy for intrusion detection and cooperative tracking, while keeping the frame rate over 20fps.
Experimental Study of Methane Hydrate Equilibria in [EMIM]-NO3 Aqueous Solutions

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Gas hydrates are ice-like crystalline compounds composed of water molecules, connected through hydrogen bonding, forming a three-dimensional lattice that is occupied by another small guest species. Hydrate formation is problematic in the oil and gas industry because the resulting pipelines blockages can lead to a major economic losses as well as flow assurance and ecological risk. To prevent hydrate formation, one common method is the application of thermodynamic and kinetic inhibitors. The former act by changing the hydrate formation conditions such that hydrates will form at much lower temperatures at the same pressures; while the latter have been developed to delay hydrate nucleation and the growth of hydrate crystals. Ionic liquids, as a new class of dual function inhibitors, have attracted much more attention. The present work is to determine the thermodynamic effect of imidazolium-based aqueous ionic liquid solutions containing 1-ethyl-3-methyl-imidazolium nitrate ([EMIM]-NO3) on methane hydrate at five mass concentrations of (5.5, 10, 20, 30, and 40) wt%. The hydrate phase equilibrium data are obtained in the pressure range of (3 to 16) MPa by using an isochoric pressure search method. The studied ionic liquid is found to behave well as a thermodynamic inhibitor on methane hydrate. The hydrate phase boundary is shifted to the higher pressures/lower temperatures. Moreover, an enhanced increase in inhibition effect is demonstrated with increasing concentrations.
Simulations of Mean Ionic Activity Coefficients and Solubilities in Aqueous Electrolyte Solutions

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We devised a method for obtaining mean ionic activity coefficients of aqueous electrolyte solutions from molecular dynamics simulations by gradually inserting ion pairs into the solution. The method is based on slow growth of the non-Coulombic part of the interactions first, followed by the Coulombic part. The infinite-dilution (reference) chemical potential of the salt is obtained by matching the simulation results at very low concentrations to the Debye-Hückel limiting law. Several common non-polarizable water and ion models were used to obtain the mean ionic activity coefficients of NaCl, KF, LiCl, LiBr, and CaCl$_2$ solutions at several concentrations at a temperature of 298.15 K and pressure of 1 bar. Gibbs-Duhem equation calculations of the thermodynamic activity of water were used to confirm thermodynamic consistency of the mean ionic activity coefficient calculations. We also tested the effect of the temperature on the mean ionic activity coefficient predictions. Deviations at high concentrations of the simulated mean ionic activity coefficients from experiment and the inaccuracies in solubility predictions necessitate the use of more sophisticated models. To this end, we are presently testing the accuracy of several polarizable ion and water models with respect to the solubility and activity coefficient predictions.
The ability to efficiently separate CO$_2$ from CH$_4$ has recently received a great deal of attention due to its importance in enhancing natural gas efficiency and in removing corrosive substances found in the raw gas stream. Nascent advancements in membrane based separations have allowed membranes to become competitive with commercial pressure and temperature swing adsorption processes. Mixed matrix membranes (MMMs) look to be the most promising candidates for commercialization and large scale implementation. These MMMs consist of three individual components: polymerizable room temperature ionic liquids (poly(RTILs), normal RTILs, and zeolite particles. These components synergize to produce enhanced gas transport. The polymer matrix allows for facile and economical fabrication, while the zeolite provides excellent separation performance. The RTIL prevents defect formation within the membrane by acting as a wetting agent to help the polymer matrix interface aptly with the zeolite. In fact, Imidazolium based RTIL materials are widely reported as great compounds for light gas separation due to their negligible vapor pressure, high thermal stability and inherent CO$_2$ solubility selectivity. We have investigated how varying the three components in our MMMs affects membrane permeability and selectivity. This initial study identified the optimal type of zeolite particles. More in depth analysis of the ionic liquid revealed the significance of molar volume in the RTIL and free volume in the poly(RTIL) on the membrane’s gas separation ability. Previous work established the correlation between increasing RTIL molar volume and decreasing CO$_2$ solubility selectivity. Current work shows how the polymerized analogues (poly(RTILs) display a similar trend with free volume. This resulted in the creation of MMMs made with smaller molar and free volume RTILs and poly(RTILs) that performed above Robeson’s 2008 upper bound for CO$_2$/CH$_4$. With this knowledge we aim to devise a systematic design approach for creating state of the art MMMs.
Scanning Thermal Microscopy (SThM) is a key promising technique for thermal measurements at nanoscale, but it remains highly non-quantitative in normal use. However, some studies reported to date showed a possibility of quantitative thermal measurements with a submicrometric spatial resolution by performing the SThM calibration with bulk materials of known thermal conductivity. The thermal conductivity values associated to these bulk materials usually come from literature, and can be therefore different depending on the bibliographic sources. It is consequently not possible to ensure the accuracy and the traceability to the international system of units of these nanoscale measurements, in particular due to the lack of suitable reference materials. To meet these needs, one task of the European project Quantiheat “Quantitative scanning probe microscopy techniques for heat transfer management in nanomaterials and nanodevices” is devoted to the thermal characterization of potential candidate materials for SThM calibration. The QUANTIHEAT project aims at solving the problems of thermal metrology at the nano-scale, especially by delivering materials and protocols for the calibration of SThM devices, and by developing numerical modelling tools for increasing the understanding of heat transfer in SThM measurements. The thermal conductivity of the bulk calibration materials are determined by LNE at 23 °C using an indirect method which is based on the measurements of the thermal diffusivity (by laser flash method), the specific heat (by differential scanning calorimetry) and the density (Archimedean method) of the studied materials. After a specification of the criteria defined to choose the more suitable materials for SThM calibration, this paper presents the materials selected, the facilities and methods used for their thermal characterization, as well as the thermal conductivity values obtained and their associated uncertainties.

Acknowledgement

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In recent years, quantum-chemical methods have become a valuable tool for the development of highly accurate interaction potentials for atoms and small molecules. Such potentials can be used to compute reference values for thermophysical properties of pure gases and gaseous mixtures for large temperature ranges by means of the kinetic theory of dilute gases and of statistical thermodynamics. Interaction energies obtained from high-level \textit{ab initio} coupled-cluster methods were used to develop accurate pair potential energy surfaces for the systems methane-nitrogen and propane-helium. We computed second interaction virial coefficients applying the Mayer-sampling Monte Carlo procedure [1] and compared the results with experimental data to verify the quality of the potentials. Furthermore, classical trajectory calculations were performed for all binary collisions involved in the dynamics of the gas mixtures under study. This included also the interaction potentials for the pure species [2-4]. The kinetic theory of dilute gases was employed to obtain the transport coefficients of the gas mixtures. We compare the theoretical results with the best experimental data for the viscosity, thermal conductivity and the binary and thermal diffusion coefficients.

References

Multistate Model of Ion Hydration

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Short range ion-solvent interaction energies are typically strong on a thermal energy scale and can rival covalent bonds in strengths, whereas the long-range interactions usually represent a collection of uncorrelated, energetically weak contributions that admit a Gaussian distribution. In developing thermodynamic models of aqueous electrolytes, one has to acknowledge these disparate scales of energy. Here we use the quasichemical organization of the potential distribution theorem to parse the short-range and long-range phenomena. The short-range contributions are recast in terms of the energetics of forming ion-water clusters within the first hydration shell and the long-range contribution is obtained using a Gaussian model of interaction energies. We use this framework to study ion hydration at infinite dilution. Using simulations based on classical (empirical) potentials, we show that for the monovalent ions studied here, only a small subset of water molecules populating the inner shell sense the chemical type of the ion. These core-water molecules also tend to attenuate the interaction of the ion with the rest of the medium, and thus the higher coordination states of the ion more sensitively reflect density fluctuations of the solvent medium at the size scale of the observation volume. This observation is used to rationalize the success and limitation of models of ion hydration that combine gas-phase modeling of ion-water clusters with approximate models of the bulk solvent. The relevance of the multistate approach in rationalizing model constants entering the semiempirical, unified theory of electrolyte solutions, a continuum-scale approach, and in informing the development of models of electrolytes based on the statistically associating fluid theory (SAFT), a meso-scale approach, is indicated.
The latent heat thermal energy storage technique is an efficient and reliable means of using phase change materials (PCMs) to store and release thermal energy, because of its large heat storage capacity, and the nearly isothermal phase change behavior of PCMs. Many organic PCMs have been investigated as latent heat thermal energy storage materials [1, 2]. A rather new material class of organic-based PCM, here termed bio-based PCMs, are significantly less flammable than paraffin. Bio-based PCMs are a type of organic fatty acid ester PCMs made from underused and renewable feedstock, like vegetable oils. So they are cheaper than paraffin, and can be mass-produced. This work presents a study on some transport properties of three commercial bio-based PCM samples supplied by RGEES LLC (http://www.rgees.com), with melting temperatures of 37ºC, 46ºC and 53ºC respectively, intended for low-temperature energy storage. The samples are mixtures of bio-based fatty acids. Experimental thermal conductivity was determined using a KD2 Pro Thermal Properties probe, whose measuring principle is the transient hot-wire method in the range 0.02-4 W·m⁻¹·ºC⁻¹. The thermal conductivity of the liquid and solid phase of the bio-PCM samples was determined, as well as the thermal diffusivity. The uncertainty of thermal conductivity determination in this case is estimated to be inferior to 3%. This paper is part of the Doctoral Thesis of D. Diez.

References

In this talk I will discuss the derivation of the postulates of statistical mechanics from the laws of mechanics and
the axiom of causality – that cause precedes effect. In order to do this we derive three main theorems: the
Fluctuation Theorem$^1$ that gives the relative probability that path integrals of the dissipation take on equal but
opposite values; the Dissipation Theorem$^2$ that relates nonequilibrium averages to time integrals of correlation
functions involving dissipation and the Relaxation Theorem$^3$ that shows how nonequilibrium systems can, under
specified circumstances, relax to that quiescent state we call equilibrium. The mathematically defined dissipation
function is central to each of these theorems.$^4$

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Influence of Latent Heat on Thermal Conductivity Measurement

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Knowing a reliable value of the thermal conductivity close to a phase transition temperature region is of great importance for many technical applications. A striking example is utilizing the phase change solid-liquid for heat storage. The thermal transport properties in such a heat storage containing a phase change material (PCM) determine the velocity of the melting process and therefore the accessibility of the stored energy. The goal of this work was to study the influence of the phase change of PCM on different measurement methods for the thermal conductivity. A transient and a steady state technique were used for the measurements, respectively the hot-wire technique and a heat flow meter. The thermal conductivity in the melting range of a PCM was determined as a function of temperature. The paraffin octadecane was used as PCM with a melting range from about 25 to 27°C. To take care of the thermal expansion during the melting process a purpose-build specimen holder was used with the heat flow meter. The experimental results show a significant variation of the measured thermal conductivity values during the phase transition depending on the used measurement technique. Even changes in experimental parameters, i.e. electrical heating power for the hot-wire method, have an influence on the measured data. For the interpretation of the experimental data, numerical simulations for the different transient and steady state measuring methods were performed taking into account the temperature dependent latent heat effects from the melting process. The experimental and the simulation data are compared and the influence of the phase change is discussed. Recommendations for good measurement practice are given in order to obtain reliable values for the thermal conductivity with both methods nearby or in the temperature region of phase transition.
Methyldiethanolamine (MDEA) is widely used for the removal of the acid gases, H2S and CO2 from gas streams. MDEA is a tertiary amine and has the advantage of being more selective for H2S removal compared to conventional amines such as monoethanolamine (MEA) and diethanolamine (DEA). One disadvantage of MDEA is its higher cost compared to conventional amines. When used in gas treating, MDEA is normally employed as an aqueous solution with a mass fraction of between 30 and 50 %. The design of suitable gas-liquid contactors requires the physical solubility of CO2. However, this solubility is difficult to determine from direct experimental measurements because the gas undergoes a chemical reaction with the solvent. Often, the physical solubility of CO2 is determined from the solubility of Nitrous Oxide (N2O) via the N2O analogy. In the present work, new data will be presented which can be used to verify the N2O analogy at high temperatures. The solubility of N2O in two aqueous MDEA solutions (mass fraction 20% and 40%) was measured at a number of temperatures in the range of 298 K to 423 K at pressures up to 2 MPa. The new experimental data paper is a part of an ongoing project to provide experimental data useful for the design of plants for the hydrocarbon-processing industry. Previous studies included the solubility of hydrogen sulfide, carbon dioxide, methane, ethane, propane, n-butane, methanethiol, ethanethiol, and propylene in aqueous MDEA solutions. Salting-in ratios, Henry's law constants, and Setchenow coefficients have been obtained from the results and will be compared with previously reported results in the literature.
The purpose of this work: thermodynamic analysis, the study of physical properties of (TlInSe2)1-x(TlGaTe2)x (x = 0-1) solid solution crystals. Concentration dependence free energy change of solid solutions is characterized by a negative deviation from the additive dependence. This agrees with the physico-chemical analysis and testifies the unlimited solubility in the solid state in TlInSe2-TlGaTe2 system. Experimental results shows the frequency dependence of ε’ for (TlInSe2)0.5(TlGaTe2)0.5 and TlInSe2 for comparison. At frequencies f = 100 kHz ε’ values of solid solution are 1.5-3.3 times higher than that of TlInSe2. ε’ value of TlInSe2 decreased by one order, and (TlInSe2)0.5(TlGaTe2)0.5 to 2.6 times with increasing frequency from 50 kHz to 35 MHz. In other words, dielectric permittivity dispersion of (TlInSe2)0.5(TlGaTe2)0.5 solid solution decreased significantly in comparison with TlInSe2. The results demonstrate that the dielectric dispersion in the studied crystals TlInSe2 and (TlInSe2)0.5(TlGaTe2)0.5 has a relaxation nature. Based on thermodynamic analysis and concentration dependence of physical properties, it was found that there is anion-cation substitution in TlInSe2-TlGaTe2 system. Frequency dispersion of real and imaginary components of complex dielectric permittivity, loss tangent and ac-conductivity of crystals of solid solutions are studied in the 50 kHz - 35 MHz frequency range. Continuous series of (TlInSe2)1-x(TlGaTe2)x solid solutions is forming throughout entire concentration range. We determined dielectric characteristics of samples, their frequency dispersion and nature of dielectric losses.
The determination of vaporization enthalpies of extremely low volatile ionic liquids is challenging and time consuming due to the low values of vapor pressure. In addition, these liquids tend to decompose already at temperatures where the vapor pressure is still low. Conventional methods for determination of vaporization enthalpies are thus limited to temperatures below the decomposition temperature. Here we present a new method for the determination of vaporization enthalpies of such liquids using differential fast scanning calorimetry. We have developed and proven this method using [EMIm][NTf2] and other less stable compounds at temperatures up to 800 K and in different atmospheres. It was demonstrated that evaporation is still the dominating process of mass loss even at such highly elevated temperatures. In addition, since the method allows very high heating rates (up to $10^5$ K s$^{-1}$), much higher temperatures can be reached in the measurement of the mass loss rate as compared to common devices without significant decomposition of the ionic liquid. We discuss the advantages and limits of this new method of vaporization enthalpy determination and compare the results with data obtained from established methods.
Wettability Measurement of Nitrided Sapphire Substrate by Ga-Al Solutions Using a Sessile Drop Method

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AlN is a promising substrate material for AlGaN-based ultraviolet light emitting diodes, because of its high thermal conductivity, high ultraviolet transmittance and small lattice mismatch with AlGaN crystal. Recently, we have developed an original liquid phase epitaxy (LPE) method using Ga-Al solution to grow AlN layer on the nitrided sapphire [1]. Using this method, a 1.2-micrometer-thick AlN layer was successfully obtained for 5 h under normal pressure [2-3]. In the case of LPE method, wettability of a substrate by a liquid is important to design the optimum growth process. Therefore, in this study, we measured the wettability of the nitrided sapphire substrate by the Ga-Al solution using a sessile drop method. To prevent oxidation of the droplet, zirconium sponges were used as an oxygen getter. Moreover, to shorten the exposing time of the droplet during experiment, the molten Ga-Al was drained out from an alumina dispenser on the substrate just before the measurement. As a result, it was clarified that the contact angle decreased with increasing temperature ranging from 700 to 1300 degree C. In the symposium, we will present the details of the results and improvement of the AlN-LPE process considering the temperature dependence of the wettability.

References

Deep saline aquifers have been identified as promising sinks for the storage of large amounts of anthropogenic carbon dioxide. In order to design safe, effective and economic carbon storage projects utilizing saline aquifers, it is necessary to have a thorough understanding of the physical and chemical properties of mixtures of CO₂ and reservoir brines at reservoir conditions. This requires a combination of empirical evidence (i.e. experimental data) and suitable models that can be applied in reservoir simulations. A survey of the literature reveals some significant gaps in the available data, especially in relation to CO₂-saturated brines at elevated temperatures and pressure. With QCCSRC, we have embarked on a program of measurements to extend the database of experimental measurements for CO₂-water and CO₂-brine systems at reservoir conditions. This has involved studies of the solubility of CO₂ in brines and measurements of the density, viscosity, pH and diffusion coefficients in the solutions. These properties have been measured over wide ranges of temperature and pressure that, in many cases, extend beyond currently anticipated reservoir conditions and provide a robust test for modelling approaches. In this lecture, I will detail the experimental approaches and results and compare the results with available models. A number of regularities emerge from the data that can be captured by quite simple models that are suitable for application in reservoir simulations.

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Designing thermodynamic processes in an efficiently and energetically optimal way requires accurate knowledge of the thermodynamic properties of the applied fluids. For this reason, there is a need for accurate equations of state. Databases alone cannot meet the increasing requirements of process engineering. Mapping the entire thermodynamic property spectrum of a given fluid is often impossible based only on laboratory experiments due to the associated financial costs, time investments, and potentially extreme measuring conditions. Therefore, only few experimental data sets are available for many fluids that are interesting for industry and science. Molecular modeling and simulation have evolved to a point of acceptance in applied sciences and are a potential solution to satisfy the need for thermodynamic data. Molecular simulation yields macroscopic properties exclusively from microscopic information. Accordingly, its predictive capabilities are, in principle, only limited by the quality of the molecular interaction model that represents the investigated substance. Therefore, molecular simulation can be used to fill gaps in experimental databases. These hybrid data sets (containing experimental and simulated thermodynamic property data) are the basis of the fundamental equations of state developed in this work. In this way, not only gaps in the experimental database are filled, but the extrapolation behavior can also be improved. This strategy was successfully applied to several different fluids, e.g., hydrogen chloride, ethylene oxide, dichloroethane, and siloxanes. All of these fluids are now described in the fluid region up to twice the critical temperature including vapor-liquid equilibrium. Based on investigations under extreme conditions of temperature, pressure, and density, the extrapolation behavior is found to be reasonable.
A Preliminary Equation of State for 3,3,3-Trifluoroprop-1-ene (R-1243zf)

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A first fundamental equation of state explicit in the Helmholtz energy is presented for 3,3,3-trifluoroprop-1-ene (R-1243zf). This refrigerant is considered as one possible replacement for 1,1,1,2-tetrafluoroethane (R-134a), because the GWP of the refrigerant is expected to be very low (approximately 10 or less), and because recent research has shown that the refrigerant exhibits similar thermodynamic behavior to R-134a. The independent variables of the equation of state are the temperature and density. All thermodynamic properties can be derived as derivatives of the Helmholtz energy. The equation of state is composed of two parts; one is an ideal-gas part representing ideal-gas properties and the other is a residual part corresponding to the influence of intermolecular forces. The ideal-gas part is analytically calculated from a correlation for the ideal-gas isobaric heat capacity. The residual part is empirically determined from experimental data for the critical parameters, vapor pressures, and liquid and vapor densities including those at the saturation state. A conventional functional form for the residual part is optimized by using a nonlinear least-square fitting to the experimental data. The final form consists of 17 terms (5 polynomial terms and 12 exponential terms). The equation is valid for temperatures from 234 K to 376 K and for pressures up to 35 MPa. Estimated uncertainties in the range are 0.1 % for the vapor pressures, 0.05 % for the liquid densities, and 0.6 % for the vapor densities. The equation shows reasonable extrapolation behavior in regions away from the experimental data. Although the equation is an interim model, it is the best currently available property representation for R-1243zf, and it provides reliable calculations of the thermodynamic properties to most technical applications.
High Pressure Density Measurements

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The petrochemical industry requires highly accurate equations of state (EoS) to calculate accurately thermodynamic properties such as densities and calorific properties. However, the accuracy of an EoS depends strongly upon the accuracy of the data used to construct the EoS. Thus, a great need exists for high accuracy \( p-V-T \) measurements. Multiple apparatus can produce highly accurate \( p-V-T \) measurements, but most cannot do so over broad ranges of pressure and temperature. With deep gas reservoirs now exhibiting pressures in excess of 140 MPa at temperatures reaching 475 K, a need exists for measurements at these extreme conditions. Two such apparatus, which can handle these harsh conditions, are a magnetic suspension densitometer (MSD) and a vibrating tube densimeter (VTD). The operating limits for the VTD and the MSD are 140 MPa and 475 K and 200 MPa and 525 K. This work presents a method to increase the rate of accurate data acquisition by using the MSD and the VTD in an optimum combination. The fluids of interest are pure fluids and natural gas-like mixtures at high pressures and temperatures. The VTD can measure densities rapidly, but the accuracy of the measurements depends upon one or more calibration fluids having accurately known densities. The MSD measurements are much slower, but accuracy of the results does not depend upon a calibration fluid. Clearly, these two apparatus used together can use measurements from the MSD to validate reference equations for calibration fluids within the VTD temperature and pressure ranges and to measure densities at higher temperatures and pressures. The VTD then adds measurements at the temperatures and pressures within its operating range. Pure fluids such as methane, carbon dioxide, nitrogen, and argon are good calibration fluids. The fluids of ultimate interest are simple mixtures of natural gas components.
The Next Generation Reference Equations of State

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Thermodynamics, and in particular Equations of State (EoS) are the cornerstones of engineering simulations. The desire to represent the available experimental data in a compact and precise manner has motivated the development of state-of-the-art multiparameter EoS. A drawback with multiparameter EoS is their computational demands with respect to time and numerical stability, for instance in phase equilibrium calculations. This has restricted their popularity, in particular for mixtures. One of the main reasons for these challenges is their behavior within the two-phase regions, where the pressure as function of density often has several artificial roots. The motivation for removing these artificial roots and obtain a "van-der-Waals like" behavior in the two-phase region has so far been almost absent. One reason for this is the misconception that properties within this region have no physical significance. Density functional theory relies on the properties of exactly this region to predict for instance surface tension, Tolman lengths, rigidity constants, nonequilibrium transfer properties, and much more. The current formulations of the reference EoS restrict the possibility to apply them for this purpose, even if the benefits of doing so may be immense. We shall in this work explain how the properties in the strongly metastable regions of a fluid can be mapped using the concept of "superstabilization". Then, we discuss how the next generation multiparameter EoS can be extended properly to the two-phase regions. We give important perspectives on the future development of reference EoS.

References

The Phase Diagrams of Simple Fluids: Ar, Kr, and CH₄ using Temperature Dependent Interaction Parameters

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Based on our past results, it is hypothesized that the use of temperature dependent interaction parameters (TDIP), instead of using temperature independent interaction parameters (TIIP), may lead to improvement in the prediction of the vapor-liquid coexistence curve. Published compilations of the second virial coefficient were used to fit a simple two parameter temperature dependent model for the collision diameter and well depth parameters of the Lennard-Jones potential energy model. Subsequently, vapor-liquid coexistence curves for argon, krypton, and methane were simulated in the NVT Gibbs ensemble Monte Carlo (GEMC). The simulations were carried out using both TDIP and TIIP. The critical temperatures and densities were determined using the Ising-scaling model. The results using TDIP produce, in general, more accurate phase diagrams compared to the diagrams generated using TIIP. The root mean square deviation (RMSD) is reduced by 42.1% using TDIP for argon. Similar reductions in RMSD were observed for Kr and methane. Also, there was no significant difference between the results obtained using TDIP and the highly accurate and computationally demanding phase diagrams based on three body contributions for argon. The phase diagram in reduced units for temperature dependent interaction parameters is a family of curves rather than a universal curve such as the case with TIIP.
Simultaneous Measurement of Conductive and Radiative Properties of SiC Foam at Temperatures up to 1200 K by Inverse Method

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SiC ceramic foam is extensively applied in the areas of thermal protection system, solar radiation absorber and porous burner, etc., because of its excellent thermal, mechanical, optical and anti-oxidation performances. The heat transports with ceramic foams include not only conduction through both solid and gaseous phases and gas convection residing in the foam pores, but also radiation. In its high temperature applications, thermal radiation dominates the heat transfer within the foam. However, limited thermal radiative properties are available, which make detailed thermal radiation analysis quite difficult. In this paper, a conductive/radiative coupled heat transfer model was developed based on radiation transfer equation and energy conservation equation for SiC ceramic foam. In combination with transient thermal distribution measurements, a simultaneous estimation of equivalent thermal properties was carried out in different temperature intervals for SiC foam by inverse method. The temperature-dependent conductive and radiative properties (i.e. extinction coefficient, albedo of scattering and linear coefficient of phase function, and conductive thermal conductivity) at temperatures up to 1200 K were obtained and discussed. The proposed analysis method provides a powerful tool for simultaneous measurements of the thermal properties at high temperatures for foams.
One of the most important and informative properties that is measured for complex fluid mixtures is the distillation (or boiling) curve. We recently introduced an improved method, called the composition-explicit or advanced distillation curve (ADC). The ADC approach addressed many of the shortcomings of the classical distillation method described above. Sampling very small distillate volumes (5 to 25 µL) yields a composition-explicit data channel with nearly instantaneous composition measurements. Chemical analysis of the distillate fractions allows for determination of how the composition of the fluid varies with volume fraction and distillation temperature, even for complex fluids. These data can be used to approximate the vapor liquid equilibrium of complex mixtures, and presents a more complete picture of the fluid under study. A limitation of the approach has been the inability to measure the liquid phase composition as part of the distillation curve. In this talk, we present a modification to the ADC in which a reflux channel is added. This modification allows direct access to the liquid composition. We will discuss results with a binary mixture (n-decane + n-tetradecane) and some preliminary measurements with diesel fuel.
Research of Thermal Stability Aliphatic Alcohols and Their Aqueous Mixtures

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The process of thermal decomposition of aliphatic alcohols (methanol, ethanol, 1-propanol and 1-butanol) and their aqueous mixtures in the range of temperatures 513.15 – 663.15 K was studied using the method of isothermal pressure increasing in a closed system. The starting temperatures ($T_H$) of thermal decomposition (decomposition points) of dissolved in water alcohols are obtained. Values of $T_H$ depending on composition ($x$) and number of carbon atom ($C$) are described by the polynomial equation $T(x,C)=23.622x^2 – 65.617x + 6.378 \times 10^{-3} C^2 + 28.826 \times 10^{-2} + 544.258$. It is shown that values of $T_H$ decrease with increasing of alcohol concentration and increase with increasing of carbon atom. The rate of thermal decomposition of alcohol molecules depending on temperature, number of carbon atoms and concentration in water is evaluated. The changes of thermal coefficients (isothermal coefficient of compressibility $\kappa_T$, coefficient of cubical expansion $\alpha$ and thermal coefficient of pressure $\beta$), and main thermodynamic properties ($C_v, C_p, H, S, U, F, G$) of studied mixtures depending on isothermal pressure increasing during the thermal decomposition of alcohols were calculated in the range of temperatures 583.15 – 663.15 K. To estimate rate of thermal decomposition of alcohols we used change of pressure of system in a unit of time at constant temperature and volume (closed system). Reaction rate constant was calculated by formula: $k = 1/p \times dp/d\tau$ where $k$ – reaction rate constant; $p$ – pressure; $\tau$ – time; $dp/d\tau$ – rate of reaction. Values of kinetic and activation parameters of alcohol decomposition in the range of temperatures 583.15 – 663.15 K are estimated.
Determination of Phase Equilibria for the Mixture (CO₂ + CH₄)

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High-pressure phase equilibrium data are often complex and difficult to predict and it is necessary to obtain some experimental data. The electric permittivity or dielectric constant is a physical property that can be defined as the electric polarization acquired by the molecules of a substance as a result of the induction generated by an electromagnetic field. It is an extensive property which depends on temperature and pressure ϵ(p,T). Based on this property has been developed a measurement technique which consists of a cylindrical resonant cavity that works in the microwave band; a sapphire tube with the sample is located inside this cavity. The resonant modes of cylindrical cavity depend on the electrical properties of the sample. For example, a liquid sample is maintained at constant temperature and the pressure is decreasing until the first bubble occurs, this phase transition presents a discontinuity in the electric permittivity and therefore in the resonant modes of the cavity. With the reverse procedure it is possible to measure the dew point. With this technique, the equilibrium data of fluid mixtures at high pressure are measured applying the synthetic method. This technique can be an alternative to the traditional visual synthetic method. The technique was checked and it has been used for measuring the phase behaviour of the binary mixture (CO₂ + CH₄) which results are presented.

Acknowledgments

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Experimental Study of the Effect of Water on the Thermodynamic Properties of Pure Components of Biogas

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As natural gas resources are declining and the European Union depends increasingly on imported natural gas, diversification of the European natural gas supply is underway. The Renewable Energy Directive 2009/28/EC requires that 20% of the European Union energy consumption should come from renewable sources by 2020. Therefore it is an urgent need to significantly increase the amount of biogas injected into natural gas networks. The diversity of the feed stocks used to produce biogas means that a large number of parameters need to be specified. This work presents the effect of small amounts of water vapor on the thermodynamic properties of pure components of biogas, such as methane and nitrogen. Experimental data on density, speed of sound and the saturation curve for mixtures of methane or nitrogen with small amounts of water, measured by means of a single-sinker densimeter, a spherical resonator and a cylindrical microwave resonator, are presented. Measurements are performed at temperatures between 250 K and 400 K, and pressures up to 20 MPa. Some related practical properties, such as the dew point and the enhancement factor, are estimated. This work is part of the project ENG54, Metrology for Biogas, of the European Metrology Research Programme (EMRP), jointly funded by the EMRP participating countries with EURAMET and the European Union. The research project receives funding from the European Community's Seventh Framework Programme, ERA-NET Plus, under Grant Agreement No. 217257.
Viscosity Measurements of Hydrate Slurries Formed from Water-In-Oil Model Emulsions

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Viscosity measurements for methane hydrate slurries were performed using a high pressure rheometer with a straight vane impeller as a stirring system. Measurements were conducted using model water-in-oil emulsions to ensure reproducibility of the results ([1]). The model emulsion consists of mineral oil 350T, water, and a surfactant mixture of sorbitane monooleate 80 (Span 80) and sodium di-2-ethylhexylsulfosuccinate (Aerosol OT, AOT). The emulsions that could be prepared with a water content (water cut), of up to 30 vol.%, are highly stable with no phase separation for up to one week, and have water droplets in the range of 2-5 µm. A general equation that describes the viscosity of the emulsion as a function of the temperature, pressure and water cut was developed. This general equation was then used as a baseline to analyze the effect of hydrate formation on the transportability of gas hydrate slurries. Results of this work are presented in terms of the viscosity of the hydrate slurry relative to the viscosity of the emulsion or continuous phase at similar temperature and pressure conditions. In addition, the results obtained in this work are compared with recent flowloop measurements. This allows further analysis and comparison between laboratory-scale rheometer measurements and large scale flowloop tests.

References

Highly Efficient Phase Change Materials (PCMs) for Building Applications

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30% of greenhouse gas emissions and 40% of the overall world energy consumption is due to the building industry [1]. The strict need to reduce global warming and energy consumption has given a strong impulse in the development of sustainable and energy efficient buildings. Amongst others, thermal storage is an effective method to improve the energy efficiency of buildings, reducing environmental impact. Traditionally, energy is stored as sensible heat, requiring large volumes. This storage volume can be significantly reduced when energy is stored as latent heat, through Phase Change Materials (PCMS). In the last years, these materials have been deeply studied, in order to try to enhance their efficiency. Amongst others, one solution is given by mixing PCMs (as paraffins) with different compounds, as metallic foams. In this work, a new generation of PCMs, made by fat acid mixed with expanded graphite (G-PCMs), is presented. This new type of PCMs allows a faster heat storage and retrieve, due to the graphite distribution inside the material that improve thermal conductivity. Here, latent heat and thermal conductivity of G-PCMs and of their base (fat acid) are compared, showing the good capabilities of G-PCMs to enhance the thermal storage in buildings.

References

The thermodynamics of electrolytes plays a key role in the design and optimization of systems ranging from refining and chemical processing to extreme deep-water oil and gas extraction. Current models have limited predictive capabilities as they rely on correlating data at moderate conditions. This limitation becomes acute when the predictions are sought at conditions very removed from conditions where model parameters were obtained, such as in extreme high temperature and pressure (HTHP) conditions of interest in describing mineral scaling and corrosion. Further, at HTHP conditions where dielectric screening is reduced, it becomes essential to acknowledge the molecular nature of the solvent and ion-solvent and ion-ion interactions. Achieving this within a consistent framework remains an outstanding challenge in both basic science and engineering. We are creating a meso-scale theory of electrolytes that draws upon molecular level insights from simulations at classical and quantum mechanical levels on the one hand and macroscopic experimental data on the other. A new statistical mechanics based model has been introduced to describe molecular aspects of ion solvation and ion-ion association. The statistical associating fluid theory (SAFT) is used to model solvent association and long-range effects are obtained using an integral equation method. Hydration shell structure with the new approach agrees well with molecular simulation results and the prediction for solution densities at HTHP shows good agreement with experimental data. We are working on refining the reference fluid for estimating packing around an ion to better describe ion-hydration with the new approach. Results from these studies will be presented. We will also discuss other extensions of the model to predict properties at HTHP conditions.
Solubility, Density, Viscosity and Heat Capacity of Mixtures of Ammonia with some Ionic Liquids for Absorption Refrigeration

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Ammonia is an excellent refrigerant for absorption heat pumps and chillers. Usually, the absorbent used for ammonia is water, but due to its low relative volatility it is required the use of rectification to separate both components after the generator, thus reducing the cooling capacity and the Coefficient of Performance COP [1]. Therefore, the use of ionic liquids (IL’s) as potential absorbents to avoid the use of rectification process has arisen recently [2,3]. Their special properties, such as negligible vapor pressure and the possibility to tailor their properties according to the application, make them a very attractive option[4]. To evaluate the performance in absorption refrigeration system, it is necessary to study the thermophysical properties of the pure IL’s and their mixtures with natural refrigerants as ammonia. In the case of ammonia, the available information of its solubility in ionic liquids is scarce[5,6], and there is no experimental information about other mixing properties. This work is focused on the measurement and modeling of some thermophysical properties such as solubility, density, viscosity and isobaric heat capacity of some ionic liquids as potential absorbents of ammonia for absorption refrigeration. The thermophysical properties of the mixtures were compared with conventional absorption refrigeration fluids.

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References

Predicting the thermodynamic properties and self-assembly of patchy colloids and of hydrogen bonding molecules (e.g., hydrogen fluoride and water) continues to be a challenge of statistical mechanics based theories. The most commonly applied approach is Wertheim’s theory and its extensions for associating particles. Most applications of the theory have considered the first order that includes only linear and branched structures, while ring formation is dominant at some conditions. The effect of bond angles on thermodynamics and structure of associated clusters is lacking in the first order theory. In addition, while most of the developments on the theory are performed with a hard sphere reference fluid, using a Lennard Jones reference makes the theory more realistic. In the work presented here, a higher order theory is developed. The effect of steric hindrance and also ring formation is included, and the equations of state derived for these systems are bond angle dependent. In our work, the bond angle refers to the angle separating the vectors connecting the centers of the two associating sites. The theory is capable of predicting the competition between ring and chain formation at various conditions. To verify the theory predictions, new Monte Carlo (MC) simulations have been performed. The theory predictions for internal energy and distribution of associated chain and ring structures as a function of bond angle are in an excellent agreement with MC simulation.
The fitted hydrate models presented in detail in part I of this contribution are in good agreement with the available experimental three phase equilibrium data up to about 100 MPa. Two phase data and hydrate composition data are represented well by the established models, too. The model results for enthalpies of formation for the gas hydrates along the three phase lines are in good agreement with experimental literature data. The developed hydrate models have been implemented in a software for the calculation of thermophysical properties, which was developed at Ruhr-Universitaet Bochum. This software is called TREND (Thermophysical Reference & Engineering Data). The most accurate equations of state available for fluid phases of pure substances and mixtures have been implemented in TREND 2.0 [1], e.g., the mixture model for CCS-relevant components by Gernert [2]. Furthermore, equations for pure solid phases [3,4] and the proposed gas hydrate models have been implemented. The phase equilibrium algorithms for fluid phases discussed in [5] have been extended to all solid phases considered in this work. Thus, up to three fluid and solid phases in equilibrium can be predicted at given temperature and pressure, pressure and enthalpy, or pressure and entropy.

References

A re-correlation of the viscosity of carbon dioxide CO₂ had become necessary for several reasons. First and most importantly, because new experimental data for the highly compressed liquid had been published which are not represented by the most recent formulation of Fenghour et al. [1]. Second, new results were published for the viscosity in the limit of zero density and for the dilute to moderately dense gas region down to near the triple point temperature. Third, Vogel reanalyzed the measurements his group had carried out in 1986 and 1993 based on recent reference viscosities. Finally, the last two correlations of Fenghour et al. and of Vesovic et al. [2] did not include the measurement results of Berg and Moldover [3] for the critical enhancement of the viscosity of CO₂. An as complete as possible compilation of the available data for the viscosity of CO₂ was attempted in this work. CO₂ is one of the most often measured fluids and the first viscosity measurements were carried out in 1846. While several of the legacy data sets are burdened with systematic uncertainties, many of them were obtained with extreme care and are in remarkable agreement with more recent measurements. A new set of data considered most reliable was assembled taking into account the theoretical advances of van den Berg and colleagues in the early 1990s regarding compressible laminar flow in capillary viscometers. The correlation was developed in two ways, both assisted by symbolic regression. The more conventional approach led to a formulation that represents the selected data with fewer adjustable parameters over a wider range of temperature and pressure and extrapolates in a physically meaningful manner. The more interaction-oriented approach uses the Frenkel-line for the transition between gas-like and liquid-like viscosity behavior. Both formulations have the potential to be models for future wide-ranging viscosity correlations for other fluids.

References

This author gave his first presentation at a Symposium on Thermophysical Properties at the ninth in 1985 which was also held in Boulder, Colorado [1]. During the 30 years since then, much guidance was published how measurements should be carried out and what techniques might be used. Needs for what should be measured derived from industrial and environmental developments such as supercritical extraction, alternative refrigerants, fossil and biofuels, and ionic liquids. These were all fit-for-purpose-and-funding campaigns but there has been little guidance for what should be measured to advance thermodynamics fundamentally. This presentation is intended to initiate a discussion of measurement strategies that are optimized for knowledge gain beyond the need of the day. Addressed will be questions such as:

Which pure fluids should be measured?
Which mixtures and at what compositions?
Which properties and combinations thereof?
Which domains of phase space need further exploration?

References

A New Implementation of the Torsional Crystal Viscometer

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Viscometry by torsionally vibrating piezoelectric quartz rods has been the only technique for absolute viscosity measurements on a routine basis. Growing needs for viscosity standards at elevated pressures and temperatures can be effectively addressed by torsional crystal viscometers without the need of calibration with reference materials. Deploying standard reference measurement methods to customers instead of standard reference materials is a new metrology priority at NIST. This talk will describe a new implementation of a torsional crystal viscosity sensor for easier assembly and thus broader usability, for higher accuracy, for an extended viscosity range, and for additional characterization of the dielectric properties of the sample fluid. This will enable the technique for measurements of species such as polar liquids and possibly electrolytes that could not be measured with this method before. Performance validation results of the sensor will be presented as they will be acquired up to the Symposium.
There is much interest in anisotropic particles adsorbed onto fluid-fluid interfaces in the context of self-assembly, surface rheology of particle-stabilised interfaces, e.g. Pickering emulsions as well as active nematics. We are interested in surface rheology, when the fluid-fluid interface has a microstructure formed by the anisotropic particles, a so-called complex interface. As a first approximation, we model anisotropic particles by hard ellipsoids and neglect capillary interactions. Non-equilibrium thermodynamic frameworks are a promising route to developing models of mechanical behaviour for many varied systems. The particular framework we use called GENERIC consists of four building blocks, which are functions of the state variables of the system we want to describe. The GENERIC building blocks are the energy, entropy, Poisson matrix and friction matrix, which combine to give a thermodynamically consistent, closed set of equations describing the whole system. We employ computer simulations and theoretical calculations for a system of hard ellipsoids confined to a plane in order to help guide the model development and extract functional forms of the building blocks. Using these, we construct a model to describe the rheology of fluid-fluid interfaces with adsorbed anisotropic particles.
Recently, refrigerants which have less impact on the environment, have attracted attention to use for refrigerators and heat pumps. Among them, Hydrofluoroolefins (HFOs) and their mixtures are considered to be leading candidates for alternative refrigerants because they have a zero ozone depletion potential (ODP) value and a very low global warming potential (GWP) value. Reliable equations of state for refrigerants are necessary to evaluate the cycle performance of refrigeration systems. In order to develop a reliable equation of state for a fluid, various thermodynamic property measurements of the fluid are required. Among them, isochoric heat capacity (cv) measurements in the liquid phase provide a very useful check for calculations of the second derivative of the pressure with respect to temperature, which is essential information to develop but is challenging to measure accurately. In this work, measured cv for R 1234ze(E), R 1234yf, and R 1234ze(Z) are examined. The measurements were carried out in a temperature range from 270 K to 400 K, and at pressures up to 30 MPa. The measured data for HFOs are carefully compared with each other, also they are compared with published equations of state.
Determination of Vapor-Liquid Equilibrium for Mixtures of Interest to the Development of Biogasolines

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The European target on decreasing the dependency on the petroleum is being achieved by the use of biofuels and it also reduces the CO2 emissions and it supports the agricultural community. There are a wide variety of biogenic products (such as alcohols or ethers) that can be added to fuels and the quality of these products becomes more and more important, requiring an accurate knowledge of the thermodynamic properties of the new fuel blends. 1-Pentanol is considered a compound of second generation biogasolines due to its high octane rating (up to 100 Research Octane Number - RON), better water tolerance and very high heat of combustion. In order to improve thermodynamic knowledge of this potential bio-additive for the conventional fuels, the VLE of the ternary system 1-pentanol + isoctane + heptane at 313.15 K has been measured. In addition, the VLE of the corresponding binary systems has been determined at the same temperature. The vapor-liquid equilibrium of these mixtures was determined using a static isothermal technique. The equilibrium properties measured directly and their uncertainties are: injected volume ± 0.03 mL, temperature ± 10 mK, and total pressure ± 5 Pa. The VLE data were correlated using and Wilson, NRTL and UNIQUAC models moreover Margules equation was used for the binary systems and the Wohl expansion for the ternary mixture.

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Link Between Molar Volume and Structure of Liquid Binary Si Alloys

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In order to investigate a link between the thermophysical properties and the structure of high-temperature melts, we have systematically analyzed concentration dependence of the molar volume and the structure factor of binary Si-M (M=Fe, Ni, Cu and Ge) alloys in the liquid state. The molar volumes of liquid alloys were obtained from their densities measured by using an electromagnetic levitation system coupled with a static magnetic field, which was developed for the measurements of various thermophysical properties. On the other hand, the structure factors were measured by synchrotron x-ray diffraction experiments with the use of aerodynamic levitation technique. While the concentration dependence of the molar volume of the Si-Ge and the Si-Cu liquid alloys obeys a linear law which is indicative of an ideal mixture, that of the Si-Ni alloys shows a large discrepancy from the linear law as well as the Si-Fe system. The liquid structure factors of the Si-Fe and the Si-Ni alloys with the concentration around 70 at.% Si indicate a correlation of medium range ordering as well as a short range ordering in the liquid alloy resulted from a strong interaction between the constituent atoms. The interaction between the constituent atoms in the liquid Si alloys was discussed with a view to analyzing the excess molar volumes, the partial molar volumes, the structure factors and the pair distribution functions.
Study of Molar Refraction and Polarisability Constant of Aqueous Solutions of KNO₃ and KBrO₃ at Different Temperatures

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Densities and Refractive Indices of solutions of potassium bromate (KBrO₃) have been studied in water and 0.1%, 0.2%, 0.3%, 0.4% and 0.5% (w/v) aqueous solution of KNO₃ with temperature in the range T = 298.15°K-313.15°K. The data obtained is utilized to determine Specific Refraction (R₀) and Molar Refraction (Rₘ) of solutions. The values of refractive indices, molar refraction (Rₘ) and molar polarizability (α) constant are found to be decreased with decreasing concentration of solute in solvent and these results are also interpreted in terms of interaction in salt solution. It has been verified that Molar Refraction is additive and constitutive property.
Atomistic Insights on the Coalescence between a Hydrate Particle and a Water Droplet within a Hydrocarbon Mixture

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The formation of hydrates can cause interruptions in the flow of oil from wells to refineries, with a substantial impact both in terms of economics and environment. To prevent the formation of hydrates, thus ensuring the continuous production of a well, the industry employs three types of hydrate inhibitors: thermodynamic inhibitors such as methanol, which shift the stability region of the hydrates, kinetic inhibitors, such as PVCAP, which are thought to both reduce the frequency of hydrate nucleation events and delay the growth of hydrate particles once formed, and anti-agglomerants, AAs, which essentially are surfactants thought to prevent the assembly of growing hydrate particles, thus preventing the formation of large agglomerates. The molecular mechanisms responsible for the performance of AAs are at present not completely understood. In an attempt to fill this knowledge gap we report here atomistic molecular dynamics simulations conducted in a system composed by decane, methane, water, hydrate, and a common surfactant, hexadecyl-trimethyl-ammonium chloride. We prepared one hydrate particle and one water droplet. We then investigated how the surfactant affects the agglomeration between the hydrate and the water droplet as a function of amount of surfactant, amount of water, and a few other thermodynamic parameters. Although the surfactant used in this study is not an effective anti-agglomerant for practical applications, the results presented could be useful for the design of novel compounds that prevent the agglomeration of hydrates in complex hydrocarbon mixtures.
We report atomistic molecular simulation results for the transport of various gases, including methane, H2S, and ethane, through narrow pores saturated by liquid water. The slit-shaped pores are of width of approximately 1 nm. This pore width is selected because the pore surface strongly affects the structure of confined water throughout the entire pore volume. Different solid materials are chosen for the pores, because they are known to affect differently the structure of interfacial water. While some materials are realistic, e.g., the cristobalite mineral of silicon dioxide, others are model ones used as proof of concept in our calculations. Equilibrium molecular dynamics simulations are used to assess the adsorption of various gases within the confined water as a function of bulk pressure. The results show that when confined water is characterized by relatively high fluctuations in density, the solubility of hydrophobic gases can be significantly enhanced compared to the solubility of the same gases in bulk water at comparable thermodynamic conditions. We analysed the free energy barriers experienced by the various gases to enter the pores saturated with water by conducting umbrella-sampling simulations, and we find that the density of water near the pore entrance determines such barriers. We then analysed the transport of the various gases within the pores using a number of statistical techniques, and we compared the selective transport of various gases through the pores filled with water. The results suggest that water could be used to enhance selectivity in membrane separations, although the permeability is reduced significantly compared to values achievable for the pores without water present.
A New Method to Derive Critical Micellar Concentration (cmc) from Surface Tension Experimental Data

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A method to derive critical micellar concentration values (cmc) from surface tension as a function of surfactant concentration experimental data at a given temperature, for systems formed by aqueous solutions of surfactants is presented. Cmc values are obtained by generating a pseudo “excess” surface tension function for which, an “ideal” surface tension as a function of surfactant concentration behavior is included. This, corresponds to a linear function obtained by considering the first experimental data (most of the time, the surface tension of pure water) and the data at the higher surfactant concentration. The “excess” surface tension function is constructed by subtracting the “ideal” surface tension at a given concentration to each experimental surface tension data along the concentration range covered. The corresponding “excess” surface tension function as a function of surfactant concentration almost always shows a well-defined global minimum which is considered to correspond to the cmc, and correspondingly, its surface tension value. To define the coordinates (surface tension and concentration) of the cmc, an analytical function to represent the “excess” surface tension as a function of surfactant concentration is constructed. In most of the cases, a polynomial function is used, from which, its first derivative equated to zero allows the definition of the coordinates mentioned. Now it is possible to obtain the cmc analytically as an extreme point!!!, avoiding the a priori elimination of experimental surface tension as a function of surfactant concentration points that is normally done using the traditional method which considers the cmc coordinates as the intersection of two lines representing the behavior shown by this property, the rapid decay and the almost constant surface tension zones. Results for different systems compared to literature will be shown, for aqueous solutions of different surfactants.
Using Molecular Simulation to Study the Interfacial Properties of CO₂/Water/Silica Systems

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Carbon dioxide capture and storage via injection into saline aquifers is a promising option for the reduction of greenhouse gas emissions and the potential mitigation of global climate change. However, the estimation of reservoir capacity has been hampered by uncertainty in key interfacial properties of the CO₂/water/rock system, especially at high pressures where supercritical CO₂ is present. In order to prevent the leakage of sequestered gas through pores in caprock, the aquifer pressure must remain below the breakthrough pressure, which depends on (1) the interfacial tension between the CO₂-rich and water-rich phases and (2) the contact angle that a water-rich droplet forms on a mineral surface in a mother CO₂-rich background. We discuss here the use of Monte Carlo (MC) molecular simulation to measure these key properties for CO₂/water mixtures in the presence of an atomistically detailed silica surface. Specifically, we present an interface potential-based free energy method to measure interfacial properties over a range of CO₂/water compositions. Results are presented for the evolution of the contact angle and CO₂/water interfacial tension over a range of pressures at select temperatures. We also discuss connections between our results and those from experimental studies.
The Fluorination Effect on the Volatility of Ionic Liquids

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Task-specific ionic liquids (TSILs) incorporate functional groups chosen to confer particular properties and to render them useful for particular applications. Fluorinated aprotic ILs are examples of task-specific ILs. The fluorination of the alkyl side-chain of imidazolium based ILs affects significantly their thermophysical properties such as density, viscosity and gas-solubility. These ILs present a high thermal stability and resistance towards oxidation and are promising due to the expected unique and specific characteristics properties associated with the fluorination. In this project, we explore the effect of cation and anion fluorination on the volatility, enthalpies and entropies of vaporization of imidazolium ILs. Electrospray ionisation mass spectrometry (ESI-MS) was used to study in detail the association of these ionic liquids to form aggregates. The vapour pressures of pure ILs were measured at different temperatures using Knudsen effusion apparatus integrated with a quartz crystal microbalance. The results showed that the fluorination of the cation and the anion increase significantly the volatility of the imidazolium ILs in comparison to their hydrogenated alkyl chain counterparts. The volatility and the thermodynamic properties of vaporization of the fluorinated ILs were analysed on the basis of the molecular interactions and structure. The ESI-MS analysis of the aggregate ion stability is in agreement with the standard enthalpy of vaporization derived from the vapour pressure measurements. It was found that the volatility increase of the fluorinated ILs is entropically driven, arising from the decrease of the molecular conformational entropy in the liquid. A parallel is established between the behaviour of these ILs and similar trends were previously observed in perfluorinated hydrocarbons.

Acknowledgements

This work was supported by Fundação para a Ciência e a Tecnologia. Ana S. M. C. Rodrigues acknowledge the financial support from Fundação para a Ciência e a Tecnologia for the award of research grant with reference SFRH/BD/81261/2011.
The possibility of controlling the polar/non-polar characteristics of ionic liquid as well as their ions shape allows the tuning of the ionic liquids properties and their use in special applications. Although several studies have been focused on the effect of the cation core, on the length of the alkyl side chain, and on the anion nature of the ionic liquid in the search for “tailored” fluids, their design by structural isomerism and aromaticity effect has received scarce attention. In this work, the vapour pressures of pure bistriflimide-based ionic liquids with different \( n \) and iso-butyl cations derivatives such as imidazolium, pyridinium, pyrrolidinium and piperidinium were measured at different temperatures using Knudsen effusion apparatus integrated with quartz crystal microbalance methodology. The thermodynamic properties, such as enthalpy and entropy of vaporization, at \( T=298.15 \), were derived. The \( n \) to iso isomerization effect and the level of aromaticity of the cation core will be used in the interpretation of the observed differentiation in their thermodynamic properties.

Acknowledgements

This work was supported by Fundação para a Ciência e a Tecnologia. Ana S. M. C. Rodrigues acknowledge the financial support from Fundação para a Ciência e a Tecnologia for the award of research grants with references, SFRH/BD/81261/2011.
Density, Speed of Sound and Refractive Index for the Ternary Systems

Di-Butyl Ether + 1-Propanol + Heptane or Cyclohexane at 298.15 K

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The increasing worldwide use of bio-fuels constitutes one of the measures considered to reduce greenhouse gas emissions. Bio-fuels also have an important part to play in promoting the security of energy supply, and promoting technological development and innovation. 1-propanol is used as blending agent in reformulated gasoline and has been included in international regulations on the promotion of the use of energy from renewable sources for transport [1]. The 1-propanol acts as non-polluting, high octane number blending agent. Di-butyl ether (DBE) is also used as blending agent in reformulated gasoline. DBE could be also used as cetane enhancer in bio-diesel fuel, and can be obtained as an added valued additive to second generation bio-fuels [3]. Recently 1-propanol has been proposed as a new alternative to conventional gasoline and diesel fuels [2]. Interest in propanols as second-generation bio-fuels has increased because they have many advantages over other potential alternative fuel candidates such as ethanol, as they can be produced from biomass by microbial fermentation of biomass (cellulose). Experimental densities, speeds of sound and refractive indexes for the ternary systems dibutyl ether + 1-propanol + heptane, or cyclohexane, and its respective constituent binary systems have been measured at 298.15 K and at atmospheric pressure. The excess molar volumes and the deviations in isentropic compressibility upon mixing have been correlated by the Redlich-Kister polynomial.

References

The crystalline structure of a solid-state material has a profound effect on its mechanical, electronic, chemical, magnetic, and optical properties. Indeed almost every practical use of a solid-state material hinges on its crystalline structure as much as its atomic makeup. Consequently, a key capability in any theory- or computation-based effort to develop new materials or to compute their properties is the ability to predict the crystalline form adopted by a given set of atomic species at a given thermodynamic state. This in turns requires the ability to compute solid-state properties with high efficiency and accuracy. Arguably our inability to do this reliably is one of the biggest obstacles to the design of new materials exhibiting desired properties. In this work we present a set of new methods to compute properties of crystalline phases. The methods are highly efficient to the extent that the modeled system is harmonic, but at the same time they do not rely on the harmonic character to produce correct results. Rather they yield data that focus strongly on characterizing the anharmonic contributions directly, so that precise results can be obtained without noise introduced from sampling harmonic effects (which can instead be characterized exactly via lattice dynamics methods). The methods are applied to several model systems, including the Lennard-Jones model, an extended Finnis-Sinclair model of bcc tungsten, clathrate hydrates modeled with the TIP4P potential, and fcc aluminum modeled using density functional theory. The approaches are shown to provide data of precision equal to that given by conventional methods, while requiring orders of magnitude less computation time.
Evaluation of New Chemicals as Tetrahydrofuran Hydrate Crystal Growth Inhibitors

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It is now well known that the most efficient chemicals to act as kinetic hydrate inhibitors are water soluble polymers, which hinder hydrate formation during enough time in order to keep adequate flow in oil and gas production activities, particularly in offshore facilities. The open literature reports good properties as low dose kinetic hydrate inhibitors for poly(N-vinylactams), poly(N-N-(di)alkyl(meth)acrylamide)s, polyvinylloxazolines, polymaleimides, polymaleamides, poly(N-vinylalkanamide)s, acrylamidopropylsulfonic acid polymers, and polyallylamides. In the present work experimental tests were performed to establish the ability of newly synthesized chemicals for perturbing and inhibiting the growth of structure II tetrahydrofuran (THF) hydrates, under atmospheric pressure and 272.65 K (-0.5 oC), with the presence of 36,000 ppm of sodium chloride to obtain an adequate subcooling temperature. The experimental method has been reported in the literature. The quantity that is used to evaluate the THF hydrate growth inhibition properties of the new chemicals, as well as that for a reference commercial chemical, is the average rate of crystal growth (g/hr) of 5 experiments for each chemical. Following the mentioned tendency three water soluble copolymers of caprolactam and alkylimidazolium were synthesized and evaluated in the concentration range (0.05 to 1.0) mass %. The experimental average rates of crystal growth show that one of those chemicals presents similar performance as the commercially available Inhibex™ 101; the latter being poly(N-vinylcaprolactam) in 2-butoxyethanol as solvent.
Micromechanical Cohesion Force between Gas Hydrate Particles Measured under High Pressure/Low Temperature Conditions

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To prevent hydrate plugging conditions in the transportation of oil/gas in multiphase flow flowlines, one of the key processes to control is the agglomeration/deposition of hydrate particles, which are determined by the cohesive/adhesive forces. Previous studies reporting measurements of the cohesive/adhesive force between hydrate particles used cyclopentane hydrates particles in a low pressure micromechanical force apparatus. In this study, we introduce a new high-pressure micromechanical force (MMF) apparatus to directly measure gas hydrate cohesive forces to measure the cohesive force of ice particles, mixed (methane/ethane, 74.7:25.3) hydrate particles (Structure II), and carbon dioxide hydrate particles (Structure I). This high pressure system has two cantilever fibers, one stationary and another controlled via a nano-manipulator. Size-controlled water droplets, approximately 500 μm in diameter, are placed at the end of the each cantilever fiber so that it can be converted into gas hydrates after the system is cooled and charged with the gas of interest. The cohesive forces are measured as a function of the contact time, contact force, temperature, and pressure, and determined from pull-off measurements based on the Hooke’s law (\( F = K_{spring} \times \Delta D \), where \( K_{spring} \) is the spring constant of the cantilever, and \( \Delta D \) is the displacement of the cantilever). For the measurements performed of the gas hydrates particles in the gas phase, the determined cohesive force is about one order of magnitude higher than that of cyclopentane particles in liquid cyclopentane.
The Thermal Near-Field: Coherence, Spectroscopy, Heat-Transfer, and Optical Forces

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One of the most universal physical processes shared by all matter at finite temperature is the emission of thermal radiation. With its origin in thermally driven fluctuations of charge carriers, thermal radiation reflects the resonant and non-resonant dielectric properties of media, which is the basis for far-field thermal emission spectroscopy. However, associated with the underlying fluctuating optical source polarization are fundamentally distinct spectral, spatial, resonant, and coherence properties of the evanescent thermal near-field. Using scattering scanning near-field microscopy we have been able to spectroscopically and spatially characterize the thermal near-field associated with molecular and surface phonon polariton (SPhP) resonances. In agreement with theoretical predictions we observe a dramatically enhanced electromagnetic local density of states (EM-LDOS) in close proximity to the sample surface. This technique of thermal infrared near-field spectroscopy (TINS) provides for broadband chemical nano-spectroscopic imaging, where the thermally driven vibrational optical dipoles provide their own intrinsic light source. Furthermore, we study the spatial and spectral characteristics of the thermal near-field SPhP response in SiC and hBN. In contrast to the strongly surface-confined thermal near-field of localized vibrational modes, an extended exponential distance dependence reflects the spatial coherence of the SPhP thermal field. In addition, we observe pronounced spectral frustration due to strong tip-sample coupling. The results highlight the possibility for local spectral and spatial tuning of the thermal SPhP resonance for control of radiative heat transfer or light-matter interaction using thermal near-field radiation.
The Phase Behavior of Solutions of Ionic Liquids

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A comprehensive review about the liquid-liquid phase behavior (LLE) of solutions of Ionic liquids of mixtures of different ILs with alcohols and aprotic polar and non-polar liquids will be given. The review focuses on different classes of systems, where in particular the influence on the LLE by a variation of the chain or even side chain length of the components has been examined, mainly mixtures of 1-alkyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)amides (CₙmimNTf₂; 1 ≤ n ≤ 14) with n-alkyl alcohols (CₙOH; 1 ≤ n ≤ 20) are considered. Partial miscibility with upper critical solution temperatures (UCST) is usually observed increasing with the chain lengths of the alcohols and decreasing with the length of the side chain of the cation. In water and diols, however, the UCSTs increase with the length of the alkyl-chains of the ILS. The numerical analysis of the phase diagrams is consistent with Ising criticality. Concepts for the description of the asymmetry of the phase diagram presuming the validity of universal scaling behavior as given by the theory of complete scaling are applied. This concept does not only allow for perfect description of the phase diagrams with a minimum of parameters but enables predictions of phase diagrams in regions that are not explored. The systematic trends of the phase behavior and the results of the analysis (UCST, critical composition, width and diameter of the phase diagrams) are discussed in detail. Comparison with the predictions of the model systems of charged hard spheres is made. The application of corresponding phase behavior on the systems investigated so far yields one single master-curve. Furthermore simple empirical relationships are formulated, that allow for the description or estimate of UCSTs of the IL-alcohol family. A simple mean-field lattice model enables rationalizing the observed regularities between size and shape of the ILs and the solvents.
Polydimethylsiloxane (PDMS) is an organosilicon compound used widely to embed electronic components, fabricate microfluidic and other MEMS/NEMS devices, and also in shampoos and lubricating oils. Most of the literature has focused on the electronic, thermal, rheological, and mechanical properties of PDMS. Though some works are reported on the optical properties, not much is known about the optical properties in the 2 microns - 15 microns range. We measured the wavelength dependent reflectivity from bulk PDMS substrates (5 mm thick) as well as thin films using an FTIR microscope. By using constrained nonlinear minimization of a least squares function to fit the bulk reflectance spectrum of PDMS with a classical oscillator function, the complex refractive index of PDMS is extracted. The emissivity spectra of PDMS thin films of various thicknesses are then predicted using said extracted properties and compared to experimental emissivity spectra from FTIR microscope measurements.
Measuring Heat Flow in Electrospun Polymer Nanowires Using the Dual Cantilever Technique

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Bi-material microcantilevers, with their high sensitivity to thermal stimuli, are well known as thermal sensors. Though they have been used for more than two decades as heat flux and/or temperature change sensors, they have only recently been used to measure thermal transport. We have designed and fabricated low thermal conductance bi-material microcantilevers by minimizing their width and thickness. Using such cantilevers, we have demonstrated heat flux resolution of less than 1 picowatt. A pair of such cantilevers is proposed as a configuration for measuring thermal conductance of a nanostructure suspended between the two. In our cantilever technique, two lasers are focused, one on each cantilever. One laser is modulated to vary the temperature at the end of one cantilever, while the second laser senses variation in heat flow through the second cantilever due to thermal conduction along the nanowire. Segments of electrospun polystyrene nanowires are suspended between the two cantilevers and the heat flow through such nanowires is quantified by measuring the cantilever deflection. Thermal conductivity of the nanowire samples is found to be between 6.6 and 14.4 Wm$^{-1}$K$^{-1}$ depending on sample, a significant increase above typical bulk conductivity values for polystyrene. The high strain rates characteristic of electrospinning are believed to lead to alignment of molecular polymer chains, and hence the increase in thermal conductivity, along the axis of the nanowire. We have designed and fabricated low thermal conductance bi-material microcantilevers by minimizing their width and thickness. Using such cantilevers, we have demonstrated heat flux resolution of less than 1 picowatt. A pair of such cantilevers is proposed as a configuration for measuring thermal conductance of a nanostructure suspended between the two. In our cantilever technique, two lasers are focused, one on each cantilever. One laser is modulated to vary the temperature at the end of one cantilever, while the second laser senses variation in heat flow through the second cantilever due to thermal conduction along the nanowire.
Mass diffusion and thermodiffusion are the two main processes governing the flux in a quiescent fluid mixture subject to a thermal gradient in the absence of convection. Oil companies show a great interest in predicting the behavior of complex fluid mixtures in well-exploitation conditions, i.e. they are interested in studying multi-component fluids, at high pressure and in porous media. In this Poster we will provide results of our recent measurements of the mass diffusion $D$ and the Soret $S_T$ coefficients of a binary mixture at different pressure levels from atmospheric up to 20MPa. The measurement involves dynamic Shadowgraph analysis of concentration non-equilibrium fluctuations allowing us detecting the mass diffusion coefficient and the solutal characteristic wave vector $q^*,s$ from which the Soret coefficient can be calculated. In order to perform these experiments a high-pressure cell has been especially developed allowing pressure control to a horizontal slab of fluid (1,2,3,4-tetrahydronaphtalene and n-dodecane, 50% w/w) of about L=5mm to which a temperature gradient is applied with an excellent temporal stability. The cell also provides optical access to the fluid parallel to the temperature gradient. The resulting values of the mass diffusion coefficient are well compatible with the Leffler-Cullinan relation as a function of the pressure, while the Soret coefficient shows a slight decrease over pressure. The calculated data points for the thermodiffusion coefficient $D_T$ are in good agreement with a previous (rare) high-pressure measurement made by means of a thermogravitational column.
Confinement Effect on the Dynamics of Concentration Non-Equilibrium Fluctuations

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It is well-known that a macroscopic gradient affects fluctuations in a fluid by making them long-ranged and enhancing their amplitude. The study of fluctuation dynamics reveals that small fluctuations exhibit diffusive lifetimes, while fluctuations larger than a characteristic size live shorter because of gravity, as theoretically and experimentally demonstrated. In this presentation we will report a combination of experimental, theoretical and numerical evidence of a dramatic slowing-down for fluctuations larger than a size dictated by the extent of the system parallel to the gradient. Results from dynamic shadowgraph experiments are complemented by theoretical calculations based on Fluctuating Hydrodynamics and previously developed to investigate the intensity of fluctuations, as well as by numerical simulations. The experimental data is found to be in excellent agreement with theory and simulations including realistic boundary conditions, demonstrating that the origin of the slowing-down is confinement.
Heat Transfer in a Rarified Air Chamber Using a Thermal Wave Resonant Cavity

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Heat transfer in gases at low pressures is an important subject in several applications, and in particular in solar thermal energy conversion, in which vacuum is used to minimize heat loses due by heat conduction. However heat transfer at low pressure involves phenomena in which the mean free path of the molecules can be very large and the usual concepts for viscous fluids have to be changed to understand transport phenomena. In this work heat transfer, in a rarefied air gas chamber is studied using the thermal wave resonant cavity technique [1]. Our experiments follow a similar methodology previously developed for the viscous regime, which was used to determine the thermal diffusivity of gases and emissivity of thin metallic foils [2]. In contrast in our case, a region of very low pressures values is explored. The thermal wave cavity is an open system, consisting on one side of a flat heat source and on the other by a flat pyroelectric detector separated by a thin layer of air. The thermal wave resonant cavity was introduced into a closed chamber and the air was evacuated using a mechanical pump. The pressure of the chamber was varied from 10^-4 to 760 Torr. In this way the heat transfer experiments were performed at low modulation frequency of the heat source and the cavity length was scanned until 1×10^4 micrometers. Our results show that in the viscous regimen to a pressure of about 1 Torr, heat transfer behaves in the usual diffusive way. However, when the pressure is lower, in such a way that the mean free path of the molecules is of the order of the size of the cavity, the experimental data obtained with the thermal wave resonant cavity, show that heat transfer is not diffusive [3,4]. The mechanisms present in all the range of pressures are presented and discussed.

References
Effect of the Presence of MEA on the CO₂ Capture of Superbase Ionic Liquids

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Recently efficient CO₂ capture and release has been demonstrated by a set of phosphonium superbase ionic liquids.¹ Further investigation of these promising results has been carried out; including the effect of modifying the cation as well as the study of other superbase anions.² In our studies both gravimetric and volumetric methods have been used to quantify and investigate the CO₂ capture of selected ionic liquid-based solutions. To date, literature studies have focused on CO₂ capture under dry conditions, however for the application of CO₂ capture from flue gas it is important to understand the effect of water on the CO₂ uptake. In this work, the effect of water on the CO₂ capture of [P₆₆₆,14][124Triz], [P₆₆₆,14][PhO], [P₆₆₆,14][Bentriz], [P₆₆₆,14][123Triz] and [P₆₆₆,14][Benzim] has been evaluated showing that depending on the anion, water can have a positive or negative effect on the CO₂ uptake.² As well as studying the effect of water, the effect of the addition of monoethanolamine (MEA) as a solvent has been investigated extensively. Currently in the literature the effect of MEA as an added solvent on CO₂ absorption has only been investigated using ILs that physically absorb the CO₂. These studies show that the MEA has no prominent effect on the CO₂ uptake however, it does have an effect on the rate of uptake.[3,4] This is due to the decrease in viscosity on the addition of a solvent. In this work, we investigated this effect when the MEA is added to ILs that chemically absorb the CO₂. Initial results have shown that generally the presence of MEA has the ability to enhance the CO₂ capture in these media suggesting that both the IL and MEA are working synergistically.

References
Effect of Impurities on the Capture of CO$_2$ using Superbase Ionic Liquids

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Recently Ionic Liquids (ILs) composed of a tetra alkyl phosphonium cation paired with a superbasic anion have been reported to exhibit equimolar CO$_2$ absorption with efficient CO$_2$ capture and release. In particular these ILs show only small changes in viscosity after reaction with CO$_2$ unlike the amino acid based ILs which exhibit large increases in viscosity. In this work the effect of water on the CO$_2$ capture of [P$_{66614}$][124Triz], [P$_{66614}$][PhO], [P$_{66614}$][Bentriz], [P$_{66614}$][123Triz] and [P$_{66614}$][Benzim] has been evaluated showing that depending on the anion, water can have a positive or negative influence on the CO$_2$ uptake. ¹ The effects of the presence or the absence of water on CO$_2$-IL interactions have been studied using $^1$H and $^{13}$C NMR spectroscopy. CO$_2$ absorption/desorption cycles have also been carried out to evaluate the recyclability of the IL as well as studies on the viscosity of the IL before and after CO$_2$ absorption under dry and wet conditions. Various methods for CO$_2$ absorption have been used and compared as well as studying the effect of changing the cation. In addition to the effect of water, studies have also been carried out looking at the effect of other impurities commonly present in industrial gas streams eg. CH$_4$, H$_2$S, NO$_x$ and SO$_x$.

References

Zinc oxide varistors are voltage-limiting ceramics devices with highly nonlinear resistance, used as overvoltage surge protection in electrical circuits. ZnO-based varistors are semiconducting ceramics fabricated by sintering of ZnO powders with small amounts of additives to enhance the non-linearity of the varistor’s behavior. The origin of their non-ohmic behavior lies in their microstructure, where ZnO grains are three-dimensionally separated from each other by grain boundary layers formed by the reactions of additives with each other and with ZnO. The electrical properties are so sensitive to the microstructure because the breakdown voltage is related to the grain size. The microstructure, electrical and thermal properties of ZnO based varistors both depend on type and content of dopant as well as the method of formulating ZnO and the processing condition [1-3]. In this work, photothermal radiometry is used to obtain the thermal diffusivity of ZnO and ZnSb2O6 performed by a traditional ceramic method and sol-gel method. Also the heat capacity and the thermal conductivity are determined. The correlation of the obtained thermal properties and the I-V response and nonlinear coefficient is investigated. The study is complemented by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

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Zinc oxide varistors are voltage-limiting ceramics devices with highly nonlinear resistance, used as overvoltage surge protection in electrical circuits. ZnO-based varistors are semiconducting ceramics fabricated by sintering of ZnO powders with small amounts of additives to enhance the non-linearity of the varistor’s behavior. The origin of their non-ohmic behavior lies in their microstructure, where ZnO grains are three-dimensionally separated from each other by grain boundary layers formed by the reactions of additives with each other and with ZnO. The electrical properties are so sensitive to the microstructure because the breakdown voltage is related to the grain size. The microstructure, electrical and thermal properties of ZnO based varistors both depend on type and content of dopant as well as the method of formulating ZnO and the processing condition [1-3]. In this work, photothermal radiometry is used to obtain the thermal diffusivity of ZnO and ZnSb2O6 performed by a traditional ceramic method and sol-gel method. Also the heat capacity and the thermal conductivity are determined. The correlation of the obtained thermal properties and the I-V response and nonlinear coefficient is investigated. The study is complemented by X-ray diffraction (XRD) and scanning electron microscopy (SEM).
Isolating the Effective Intermolecular Potential for Water-Alkane Interactions from Water Solubility: Implications for Theory and Simulation

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Intermolecular potential models for water and alkanes describe pure component properties fairly well, but fail to reproduce solubility of water in alkanes. Understanding interactions between water and non-polar molecules like alkanes has important implications for flow assurance in gas processing and oil production as well as in biological processes. Although non-polar solutes in water have been widely studied, much less work has focused on water in non-polar solvents. We use molecular simulation and the SAFT model to calculate the solubility of water in different alkanes (methane to dodecane) at ambient conditions where the water content in alkanes is very low so that the non-polar water-alkane interactions determine solubility. Only the alkane-rich phase is simulated since the fugacity of water in the water rich phase is calculated from an accurate equation of state. Using the SPC/E model for water and TraPPE model for alkanes along with Lorentz-Berthelot mixing rules for the cross parameters produces a water solubility that is an order of magnitude lower than the experimental value. It is found that an effective water Lennard-Jones energy \( \varepsilon_{W}/k = 220 \) K is required to match the experimental water solubility in TraPPE alkanes. This number is much higher than used in most simulation water models (SPC/E: \( \varepsilon_{W}/k = 78.2 \) K). It is surprising that the interaction energy obtained here is also higher than the water-alkane interaction energy predicted by studies on solubility of alkanes in water. The reason for this high water-alkane interaction energy is not completely understood. Some factors that might contribute to the large interaction energy, such as polarizability of alkanes, octupole moment of methane, and clustering of water at low concentrations in alkanes, are examined. It is found that, though important, these factors do not completely explain the anomalously strong attraction between alkanes and water observed experimentally.
Ultrafast Heat Transfer in Nanoscale Materials

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On the macroscopic lengths scales of conventional engineering systems, heat transfer by conduction is generally a slow process well-described by the heat diffusion equation. The characteristic time-scale of diffusion scales with the square of length; therefore, at nanometer length scales, heat conduction can involve processes that occur on time-scales of picoseconds, i.e., a few trillionth of a second. We use ultrafast pump-probe optical techniques to directly study a variety of unconventional heat transfer mechanisms that are critical in nanoscale devices and nanoscale materials. Our studies encompass a diverse variety of systems (metallic nanoparticles for photothermal medical therapies, phase change materials for solid-state memory, and heat-assisted magnetic recording) and physical mechanisms (the thermal conductance of interfaces between dissimilar materials, the non-equilibrium between thermal excitations of electrons, phonons, and magnons, and the cross-terms in the transport of heat, charge, and spin). In this talk I will highlight three recent examples: i) ultrafast thermal transport in the surroundings of plasmonic nanostructures; ii) limitations on ultrafast heating of metallic multilayers imposed by electron-phonon coupling; and iii) the generation of currents of magnetization by the spin-dependent Seebeck effect and extreme heat fluxes exceeding 100 GW m⁻².
For the calibration of some infrared cameras and radiation thermometers with large fields of view, it is useful to have radiators that have emitting areas with diameters larger than those of the typical apertures of blackbody cavities. Because Flat plate calibrators have such large areas, they are used in many calibration laboratories. It is a normal procedure to calibrate them radiometrically in a given spectral range (typically the 8 to 14 micrometer wavelength range) because their radiant surfaces do not have the emissivity of a blackbody, nor of a gray-body. This procedure makes it possible to use them to calibrate radiation thermometers working in that wavelength range without needing to know the actual spectral emittance of the calibrator. If a flat plate calibrator is to be used to calibrate radiation thermometers that work in different wavelength ranges, then it is necessary to know its spectral emittance to make the appropriate corrections to the measurement results. For this purpose, an emittance measurement facility based on a Fourier Transform Infrared Spectrometer was developed at Centro Nacional de Metrologia (CENAM, Mexico). In 2011, the spectral emittance of a brand new flat plate calibrator was measured, and it was re-measured after three years of usage. It was found that there was a change in the spectral emittance of the calibrator: 0.8% in the 8 to 14 micrometer wavelength range, and more than 3 % in the 5 to 8 and 14 to 25 micrometer wavelength ranges. In this work, the measurement results are presented.
Theoretically Based Ion Potential Models in Molecular-Based Electrolyte Equations of State for the Prediction of Solvation Energies

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Thermodynamic modelling of electrolyte solutions using a molecular-based equation of state (EOS) is challenging due to the complexity and range of the molecular forces: short-ranged repulsion; mid-ranged dispersion; directional hydrogen-bonding; and long-ranged Coulombic interactions. A thermodynamic perturbation approach, such as SAFT, is ideally suited to meet this challenge since its construction allows one to incorporate independent contributions to the free-energy expression, however the additive nature of the expression introduces many parameters. SAFT-VRE Mie is an extension for electrolytes of the SAFT-VR Mie [1] EOS. The Mie potential is used to represent the short-ranged repulsive, and dispersive (attractive) interactions. Coulombic interactions are incorporated at the unrestricted-primitive-model level, using Debye-Hückel [2] theory, or the MSA [3]. Physically sensible ion potential parameters are obtained from well-known physical quantities, incorporating literature values of ion diameters [4], ion-solvation diameters, and the polarizabilities of ions, using the approach of Hudson and McCoubrey [5]. Only a single solvent-ion interaction remains to be obtained from available fluid-mixture experimental data. This single-parameter approach retains near equal performance to the more-common three-parameter schemes. Our approach vastly simplifies the parameter space of the EOS; it also allows for the direct comparison of chemical potentials at the limit of infinite dilution through quantitative prediction of solvation energies in aqueous solutions.

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Rigorous approaches to the fluid-fluid interfacial tension (IFT), such as the family of density functional theories [1], provide predictive insight into the thermodynamics of the interface. However, such approaches are computationally intensive and scale badly with the number of components when applied to mixtures. One alternative is the square gradient theory (SGT) [1]. This reduces the computational effort but adds a free parameter, the influence parameter, CIP, making the theory non-predictive – a fact only partially mitigated by model-specific correlations of CIP. In this work we develop a predictive SGT by means of the molecular model underlying SAFT-VR Mie [2].

The free energy is described within an SGT formalism, in which CIP has a straightforward link to the direct correlation function (DCF) of the fluid. We propose a simple approximation for the DCF of a Mie segment. Together with detail of the molecular model, and by means of an effective mapping in state variables, this provides a predictive, closed-form expression for CIP, which can be used in the normal SGT formalism, together with SAFT-VR Mie, to calculate the IFT of single-segment molecules. The mapping is calibrated for a range of Mie potentials using IFT data from molecular simulations of Mie spheres. Extension of the approach to multi-segment chains, and to mixtures, is straightforward.

We test our approach by predicting the IFT of Mie fluids not included in the calibration, and demonstrate its predictive power through the calculation of IFTs of multi-segment Mie-chain molecules, as well as real fluids.

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The thermal conductivity of \( x\text{CH}_4 + (1-x)\text{C}_3\text{H}_8 \) with \( x = 0.949 \) was measured at temperatures from (200 to 423) K and pressures between (10 to 31) MPa, using an transient hot-wire method. The measurements were conducted with a recently constructed transient hot-wire instrument. Two 12.5 μm diameter platinum wires of length 23 mm and 57 mm were arranged in opposite arms of a Wheatstone bridge in order to eliminate the end effects arising from axial conduction. These new data on transport properties of natural gas mixtures will assist to achieve more efficient designs of industrial processes and equipment. The data acquisition system (capable of multi-channel sampling at 1 MHz) interrogated several voltages in the circuit simultaneously. The pressure transducer and platinum resistance thermometer were calibrated before the measurement, and the resistances of the two platinum wires were determined as a function of temperature. Performance of the instrument was verified by measuring the thermal conductivity of nitrogen and helium over a range of temperatures and pressures. The results for the thermal conductivity of \( x\text{CH}_4 + (1-x)\text{C}_3\text{H}_8 \) with \( x = 0.949 \) are compared with the limited literature data [1, 2] and values predicted from the extended corresponding states model implemented in REFPROP 9.1 by plots of deviations from that model.

References

Monte Carlo Simulations for Water/N-Alkane/1-Alkanol Mixtures

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Multi-component mixtures that exhibit a liquid-liquid miscibility gap are of utmost importance for the oil and gas industries because of the prevalence of hydrocarbons and water in many processes. Here we present configurational-bias Monte Carlo simulations in the Gibbs ensemble to investigate the phase behavior and structure of ternary water/(n-hexane or n-dodecane)/(ethanol or 1-propanol) mixtures. Analysis of the simulation trajectories yields a wealth of information on microheterogeneous features of the liquid phases.
Ultrathin Film Absorber for Solar Energy Conversion Systems

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Trade-off between the thickness and optical absorption of an active layer is critical for solar energy conversion systems. Thinner active layers are needed to reduce the cost of these systems or required due to poor carrier transport abilities. Kats et al. (Nature Materials, 2013, 12: 20-24) recently demonstrated a new type of absorber comprising an ultrathin absorbing dielectric layer coated on a metallic substrate with finite optical conductivity. The absorbing layer is only a few to tens nanometers in thickness which is much thinner than conventional optical coatings. However, this absorber shows narrowband absorption but broadband absorbers are much more useful. Here, we presented two strategies to achieve high broadband absorption in ultrathin films. First, the effective medium design strategy was used to achieve destructive interference over a broad spectrum to realize a solar thermal absorber. This strategy was experimentally and theoretically demonstrated with an absorber having 5 nm Ge, 10 nm Ti and 50 nm SiO₂ layers coated on an Ag substrate fabricated by a simple deposition method. The absorptivity of higher than 0.8 was achieved in the 15 nm thick Ge and Ti films from 400 to 950 nm. Secondly, destructive interference and surface plasmon resonance were combined to realize a solar water splitting absorber. This strategy was theoretically demonstrated with an absorber having 20 nm hematite planar film, a dielectric filled silver nanohole array and a silver substrate. This absorber has both high absorption comparable to nanophotonic structures due to supported destructive interference and surface plasmon resonance, and lower recombination loss characteristic of planar ultrathin films.
High Refractive Index Photonic Crystals for Simultaneous Enhancement and Redistribution of the Spectral and Directional Thermal Radiation

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Outstanding control of thermal radiation properties is significant in many energy conversion processes including solar-thermal, solar-photovoltaics, solar-thermochemical and solar-thermophotovoltaics. The radiance, $E$, at a wavelength, $\lambda$, in a direction, $\theta$, is the most fundamental quantity in thermal radiation. The blackbody hemispherical radiance over the entire spectrum obeys the well-known Stefan-Boltzmann law along with the Planck spectral distribution and the Lambertian directional distribution. Many studies have sought to enhance the thermal radiation in the far-field regime and the near-field regime or to tailor the spectral and directional radiance distributions. Here, we present general guidelines to design photonic crystals using transparent materials with high refractive index. Such photonic crystals are used to simultaneously enhance the thermal emissions and redistribute the spectral and directional radiation distributions. We observed an $n^{0.80}$-fold enhancement ($n$ is the refractive index) of the blackbody hemispherical radiance and an $n^{1.04}$-fold enhancement of the blackbody normal radiance to the far-field vacuum at the selected wavelength where the vertical mode of the photonic crystal matches the destructive mode. In this case, the blackbody is modified to a wavelength selective thermal emitter with enhanced hemispherical and normal radiation fluxes. Our results shed light on applications of high refractive index materials in harvesting solar energy.
Anisotropic Thermal Property Measurement of a Polymer Composite by using the 3 Omega Method

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Polymer composites having thermal conductivity comparable to stainless steel (16 Wm⁻¹K⁻¹) are commercially available nowadays. Additives with superb thermal transport characteristics such as carbon nanotubes, graphene and etc. are added to base polymers to achieve up to 2 orders of magnitude increment in thermal conductivity. Thermally conductive polymers are expected to replace metallic frames of advanced heat exchanging systems that needs light weight and chemical inerntness. However, in such polymer composites, the weight fraction of additive becomes comparable or even overwhelms the portion of base polymer. High loading of additives can cause problems such as inhomogeneous additive distribution leading to non-uniform and anisotropic thermal conductivity within the product. Often, thermal analysis techniques are used to analyze the effects of additive distribution but quantitative measurement is extremely difficult since the additive orientation inside a composite is a complicated function of measurement sample configuration, manufacturing method, thermal history and etc. In this paper, a modified 3-omega method is utilized to assess the additive orientation in a polymer composite sample. Thermal conductivity measurement by using microheater and temperature sensor arrays provide information of in- and through-plane thermal conductivity of a polymer composite with spatial resolution smaller than 1 mm. Localized thermal conductivity measurement results are used to analyze the additive concentration distribution within the sample and assess the additive mixing characteristics.
Densities / volumes are among the most commonly reported physicochemical properties of aqueous electrolyte solutions in the chemical literature. Apart from their intrinsic value, volumetric information is useful for calculating changes to electrolyte activity and solubility when systems are subjected to high pressure, such as occurs in seawater and deep geological brines. While the major sea salts have been the focus of many experimental studies at high pressure and over a range of temperature, unfortunately, reliable density information for most other salts is lacking for conditions away from ambient. Thus, there is a need for well-founded approaches to estimating the volumetric properties of aqueous electrolyte solutions and their mixtures as functions of pressure and temperature. This work describes an investigation into methods of obtaining solution densities in both the temperature and pressure domain based on (i) having limited numbers of experimental data available at 298 K and 0.1 MPa, and (ii) empirical trends that have been observed for the best-characterized electrolyte solutions in the pressure and temperature range of interest. The predictions are validated against authoritative volumetric data for binary and multicomponent electrolyte solutions at pressures up to 100 MPa and temperatures from (273 to 373) K.
The National Institute of Standards and Technology (NIST), in cooperation with the Advanced Research Projects Agency–Energy (ARPA-E) of the U.S. Department of Energy, has developed a web-based database for cataloging adsorbent materials and curating data regarding adsorption of gases by those materials. This new Standard Reference Data product is intended to be used to disseminate data and properties of the cataloged adsorption systems for use by groups across disciplines and sectors, including industry, academia, instrument manufacturers, standards bodies, and government laboratories. Interested parties can access this tool for comparison with their own measurements, to test and calibrate equipment, or to screen adsorbents and adsorbates for desired behavior or properties. The data for adsorbent materials, adsorbate fluids, and their interactions are obtained from open sources in the scientific literature and measurements at participating laboratories, including the NIST Facility for Adsorbent Characterization and Testing. In this work, we present the new database and web application to the gas adsorption community and discuss its goals, both to advertise the new resource and to foster conversations that will improve the goals and future direction of the work so that it is a truly beneficial to the broad community studying adsorbent materials and those utilizing porous materials for end applications. We also discuss pitfalls encountered while gathering adsorption data from the scientific literature related to inconsistencies and common errors in data presentation. These difficulties, however, have also identified opportunities for standardizing the presentation of adsorption data, which could greatly aid comparisons of adsorption data from different laboratories as well as ease the inclusion of newly-measured adsorption data into the NIST database. Finally, we discuss other opportunities for improving the presentation and dissemination of adsorption data, including the introduction of a standard isotherm format, community submissions to the NIST database, and indexing/cataloging of adsorbent materials.
On Adsorption Hysteresis in Closed-end Pores: Isotherm Reconstruction and Free Energy Analysis via Flat-histogram Monte Carlo Simulation

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In studies of the thermodynamics of fluids confined in porous materials, a particularly interesting observed effect is that of adsorption-desorption hysteresis at subcritical temperature. This effect was observed and remarked upon nearly a century ago[1] and has been a point of discussion and, occasionally, contention ever since. An early explanation of hysteresis based on macroscopic thermodynamics, the Kelvin-Cohan relationship, proposed that the effect resulted from the formation of different gas-liquid menisci during the respective adsorption and desorption processes[2]. Later investigations linked hysteresis to fluid metastability and confirmed this argument via statistical mechanical means. Based on the Kelvin-Cohan relationship, it was long assumed that hysteresis would not occur in a closed-end pore because the meniscus would be identically structured in the adsorption and desorption processes[2]. Some molecular simulations suggested the existence of hysteresis in a closed-end pore, but the uncertainty in the data precluded a firm conclusion[3]. More recent work by Do and coworkers has more confidently revealed the existence of hysteresis in closed-end pores of various shapes[4] via molecular simulations. Despite these results, disagreement over the existence of hysteresis in closed-end pores still persists in the field. In the present work, we examine adsorption-desorption hysteresis in closed-end pores using flat-histogram Monte Carlo methods, in particular hybrid Wang-Landau/Transition-matrix Monte Carlo simulation. As we demonstrated recently[5], TMMC can easily and accurately compute adsorption isotherms exhibiting hysteresis including identification of the metastable regions, with high confidence. We now apply this method to adsorption in closed-end pores with the intention of verifying the results of Do and coworkers, as well as examining the purported metastable regions via ensemble macrostate probability distributions and free energy analyses.

References

As a structure I crystal former, ethane hydrates share fundamental nucleation concepts with methane hydrates, beginning with the formation of coordinated guest clusters in water. However, while methane demonstrates total occupancy of structure I, which contains two $5^{12}$ and six $5^{12}6^7$ cages in its unit cell, ethane will only infrequently occupy the $5^{12}$ cages. Indeed, observations from molecular dynamics simulation studies reveal that there exist differences in both the cage type distributions and cage occupancy between methane and ethane hydrate nucleation. Occupied $5^{12}$ cages dominate methane hydrate nucleation, while ethane hydrates have been found to predominately form $4^{15}10^6$ cages as both the first and most common cage structure. While the $4^{15}10^6$ cage appears to provide a more comfortable fit for the ethane molecule than the $5^{12}$ cage, the orientation of the coordinate guest ethane molecule appears to be restricted inside the $4^{15}10^6$ cage. These $4^{15}10^6$ cages do not represent thermodynamically stable structures, and thus are not observed to occur in the crystal structure. However, these kinetically favored cages have been observed to readily undergo transformation into different thermodynamically favored cage structures, such as $5^{12}$ or $5^{12}6^7$ cages. These results have been obtained from a number of NPT molecular dynamics simulations of water and ethane, starting from phase separated systems corresponding to a bulk water and bulk ethane phases.
Systematic and Simulation-Free Coarse Graining of Polymer Melts

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Full atomistic simulations of many-chain systems such as polymer melts are not feasible at present due to their formidable computational requirements. Coarse-grained (CG) models have to be used instead, where each segment represents, for example, the center-of-mass of a group of atoms/monomers. Such models, however, reduce the chain conformational entropy, which plays an essential role in the thermodynamic behavior of polymeric systems. On the other hand, in most work on coarse graining, molecular simulations are used to obtain the structural and/or thermodynamic properties of both original and CG systems that need to be matched, which is not only computationally very expensive but also non-transferable. Here we present a systematic and simulation-free strategy for both structure- and relative-entropy-based coarse graining of homopolymer melts. We use integral-equation theories, instead of molecular simulations, for both original and CG systems, and examine in detail how the CG potential varies with \( N \) (the number of CG segments on each chain) and how well the CG models can reproduce the structural and thermodynamic properties of the original system. The structure-based approach reproduces the structural but not thermodynamic properties of the original system due to the information loss of coarse-graining, and the relative-entropy-based approach minimizes such information loss. Our systematic and simulation-free coarse-graining strategy is much faster than those using molecular simulations, and provides a quantitative basis for choosing small \( N \)-values that can still capture the chain conformational entropy, a characteristic of polymers.
Clathrate hydrate are solid crystalline compounds most commonly formed from solution to nucleate a mixed solid composed of water and gas. Understanding the mechanism of clathrate hydrate nucleation is crucial for a fundamental study of formation of these complex structures and their applications. Molecular Dynamics (MD) simulation is an ideal method to observe nucleation at the molecular level because the size of the critical nucleus and the nucleation time are nano scales. Various analysis methods have been developed through MD simulations to analyze nucleation in monatomic systems. In particular, the nucleation rate, the critical nucleus size, and the free energy curve can be obtained from mean first-passage time, survival probability, and Yasuoka-Matsumoto methods. However, clathrate hydrate nucleation is difficult to observe in MD simulations due to high free energy barriers, so these methods have not been applied to clathrate hydrate systems. Recently, methane hydrate nucleation has been observed by MD simulations at 255 K and 50 MPa using high performance computing. In this study, we analyzed methane hydrate nucleation using these methods for data generated from MD simulations and verified the applicability of these methods for the methane hydrate nucleation analysis. These methods are also easily applicable to other complex clathrate hydrate structures.
Competitive Effects of Chemicals on Hydrate Particle Cohesion

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In oilfield production conditions, many chemicals are present, both in the form of natural surfactants that are present in the oil phase, as well as additives that are injected to control the properties of the oil phase. These additives may include Low Dosage Hydrate Inhibitors (LDHIs) such as Kinetic Hydrate Inhibitors (KHIs) or Anti-Agglomerants (AAs), corrosion or scale inhibitors, dispersants, etc. In order to achieve slurry flow in subsea oil pipelines, the agglomeration of hydrate particles needs to be minimized so that the small, dispersed hydrates are transportable rather than forming larger aggregations that may plug the pipeline. This study focuses on the interactions of several classes of chemicals on the cohesion force between two hydrate particles. A Micromechanical Force apparatus was used to measure the changes in the cohesion force for cyclopentane hydrates when a dispersant, a KHI, and a model AA are added to the cyclopentane phase. The cohesion force is tested for individual chemicals, as well as when multiple chemicals are present. It was found that the interaction of specific chemicals can work synergistically, where the effect is greater than either additive can produce on its own, or antagonistically where the effect is reduced for the chemical mixture, or show no interaction where the cohesion force is similar to when only the more effective chemical is present.
Accurate measurement of the thermophysical properties of new, exotic carbon composites is critical in their design process. Researchers are targeting a carbon-based material with a rising thermal conductivity when subjected to increasing temperatures, with an extremely low thermal expansion coefficient through this temperature range. Through the initial Research & Development stage, fast and accurate measurement of these parameters helps to delineate different approaches to achieving the desired materials mechanical and thermal properties. The use of the modified transient plane source (MTPS) method provides for a powerful and quick way to determine the thermal conductivity in complex carbon composite materials. Thermal expansion is measured with a high-resolution interferometer. The accuracy of both methods is verified in testing certified reference materials. Ranking of a variety of carbon composite samples through a range of temperatures is presented. Thermal conductivity is measured over a temperature range of 25 to 200°C, and thermal expansion from room temperature to 1000°C.
Describing the Transport of CO$_2$ through a Cellulose Acetate Membrane with Non-Equilibrium Thermodynamics

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Membranes are nowadays part of a mature technology for purification of natural gas from CO$_2$. Numerous alternatives are available for that purpose. However, due to its features, the membrane technology is particularly interesting when combined with enhance oil/gas recovery, since it allows overcoming the inherent drawback of low selectivity. In such processes, the different composition of the raw gas and operating pressures determine the overall performance and operating cost of the process. Therefore, the development of proper permeation models is an important issue. Engineering models typically account for phenomena such as concentration polarization [1], coupled transport [2], or the composite structure of the membrane using global transport parameters. The limitation is that the parameters will often depend on the operating conditions and the system parameters in non-trivial ways. To gain a proper insight on the permeation of the gas, all the different involved steps should be considered [3]. First, the gas diffuses through the boundary layer at the feed side, and it is absorbed in the surface of the membrane. Then, it diffuses through the active dense layer, to be desorbed at the interface with the porous support layer. Finally, it is transported through the support to the feed side, where it diffuses to the bulk phase. All these steps constitute a relevant resistance towards the permeation of the gas. It should be noticed that due to the large pressure difference between the feed/residue side (typically above 50 bar) and the permeate side in the membrane unit, there will be significant Joule-Thompson effects as gas moves across the membrane [4]. The theory of non-equilibrium thermodynamics combined with a proper description of thermodynamic properties [5-6] enables us to accurately describe the mentioned phenomena, and possibly evaluate the impact on the performance and costs of the membrane unit.

References

Bubble Point Measurements on Butane-Octane and Butane-Nonane Binary Mixtures

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Mixtures of small gaseous hydrocarbons with longer chain hydrocarbons are of interest to the natural gas industry. Mixtures containing nonane are of particular interest, as nonane was just incorporated into the GERG-2008 equation of state. The bubble-point pressures of three compositions of each of the binary mixtures butane-octane and butane-nonane were measured over the temperature range of 270 K to 370 K. Bubble-point data are reported and compared to existing literature data as well the GERG-2008 equation.
Small Volume Apparatus for Vapor Liquid Equilibrium Measurements

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Vapor liquid equilibria data are cornerstone to the development of accurate equations of state for the prediction of thermophysical properties. Previously, the design of a small volume phase equilibria apparatus at NIST was reported which allowed for measurements on hazardous materials and small volume samples. A new apparatus has been developed incorporating improvements on the previous design to allow for better temperature control and improved uncertainty. The temperature range of the apparatus is 260 K to 380 K and pressures up to 10 MPa.
Levoglucosan (1,6-anhydro-\(\beta\)-D-glucopyranose) is a carbohydrate formed during thermal decomposition of cellulose and cellulosic materials. It can be used for production of biodegradable polymers, antibiotics and other materials. In this work, we present the results of the comprehensive study of thermodynamic properties for this substance. Heat capacity of levoglucosan was measured over the temperature range (5 to 370) K by adiabatic calorimetry. The temperatures and enthalpies of a transition into the plastic crystal phase and fusion determined by DSC were in good agreement with literature. The obtained results allowed us to calculate thermodynamic properties of crystalline levoglucosan in the temperature range (0 to 384) K. Enthalpy of sublimation for the low-temperature crystal phase was derived from the temperature dependence of saturated vapor pressure from the Knudsen effusion method. Thermodynamic properties of levoglucosan in the ideal-gas state were found by methods of statistical thermodynamics using molecular parameters from quantum chemical calculations. A theoretical value of the standard entropy at \(T = 370\) K for gaseous levoglucosan agreed well with that derived from the experimental data. Enthalpy of formation of the crystalline compound was found from experiments in a combustion calorimeter. The gas-phase enthalpy of formation obtained at the G4 level of theory was too negative compared to that found from the experimental data even if isodesmic reactions were used. Thermodynamic analysis of equilibria of levoglucosan formation from cellulose, starch and glucose demonstrated that this process is possible only if the product is formed in the gas phase and then quickly removed from the reaction zone.

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A collaboration of five European National Metrology Institutes (NPL, CMI, LNE, MKEH and PTB) is working on the project SIB52 "Metrology for thermal protection materials" (Thermo) of the European Metrology Research Programme (EMRP). One of the objectives of this project is to enable thermal conductivity measurements of thermal protection materials at temperatures up to 800 °C with an uncertainty better than ±5 %. The guarded hot plate method is a well-established steady-state technique to measure the thermal conductivity. While at room temperature the results of measurements performed on thermal protection materials at different locations with different apparatuses agree very well, at higher temperatures the results show considerable differences. One source of errors may be found in the complex nature of the heat transfer in thermal protection materials that are mostly porous and occasionally semi-transparent. At room temperature the heat transport is dominated by conduction whereby at higher temperatures the contribution of radiation to the overall heat transfer increases significantly. By means of theoretical modelling the radiative part of heat transfer in thermal conductivity measurements of thermal protection materials performed with a high-temperature guarded hot plate apparatus was investigated. The amount of the radiative heat transfer through highly porous semi-transparent samples as well as the radiative heat losses of the measuring instrument were modelled by finite element method. The investigation includes experimental measurements of the relevant thermophysical and optical properties. The results of the numerical simulation will be presented in comparison to appropriate analytical calculations.

Acknowledgements

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Gas hydrates are crystalline structures of water stabilized by light natural gas molecules. Increased understanding of hydrate deposition and other hydrate formation mechanisms in oil and gas pipelines can result in reduced risk for hydrate blockage, reduced inhibitor injection and, in some cases, lead to introduction of new hydrate management strategies for decreasing operational costs. This paper presents results from experimental measurements of hydrate formation in a rocking cell setup with visual capabilities. The constant volume experiments were performed at initial pressure of 38 bar and temperature of 20 °C and then cooled to stable hydrate conditions. 42% of the cell volume was filled with fresh or saline water, 28% with gas condensate or mineral oil, and the rest was gas phase containing a methane/ethane mixture. Pressure and temperature were measured during the experiment to enable calculation of amount of water converted to hydrates. Windows in the side wall of the rocking cell facilitated video recording of the hydrate formation process. Hydrate growth both in the bulk and on the surface, sloughing of hydrate deposit, bedding of hydrate particles in a hydrate slurry and conversion of bedded particles to hydrate deposits were some of the mechanisms identified. Prior to hydrate formation, phases were dispersed, and upon hydrate formation onset the liquid phases appeared to completely separated until some visible amount of hydrates had formed. This phenomenon is fundamentally intriguing and potentially of significant practical interest. It might be explained by the sudden change in fluid properties, such as viscosity, density and interfacial tension of the oil phase due to fast gas uptake in initial formation of hydrates. Another proposed explanation could be that the hydrate particles forming at the oil/water interface destabilize emulsions due to the hydrate surface energy properties, similarly to how clay particles stabilize a Pickering emulsion.
Pyrolysis oil is considered as an alternative energy resource for fossil fuels. However, the pyrolysis oil must be upgraded before it can be used as fuel. The upgrading and subsequent downstream processes in the biorefineries require accurate thermodynamic models of the compounds formed during pyrolysis. These models rely on the accurate data of the thermophysical properties of the pyrolysis oils components. Our literature review of the thermodynamic data revealed a large gap on experimental data of the thermophysical properties such as vapour pressure, enthalpy of vaporization, and enthalpy of combustion. For that purposes, a new Knudsen effusion apparatus was built in our laboratory and tested by measuring the vapour pressures of the reference organic compounds such as benzoic acid and anthracene in the temperature ranges 299-317 K and 340-360 K, respectively. A commercial bomb calorimeter Parr-6200 was tested for measuring the enthalpy of combustion of anthracene. Benzoic acid was used to determine the energy equivalent of the calorimeter and to test precision and accuracy of the equipment. From the value of the standard specific energy of combustion, the standard molar enthalpy of combustion and the standard molar enthalpy of formation in the liquid state can be derived. The first relevant compound identified in the pyrolysis oil that measured in this work is 5-(Hydroxymethyl)furfural. It is one of the major components found in the pyrolysis of cellulose and also very important intermediate compound for the production of the biofuel dimethylfuran (DMF), as well as for the production of other molecule such as levulinic acid. In this work, the vapor pressures and enthalpy of vaporization of 5-(Hydroxymethyl)furfural are presented. The ongoing measurements on vapor pressures and enthalpy of combustion of the major compounds existing in pyrolysis oil are expected to get underway in the future.
We propose an extension of the improved version of the inhomogeneous long-range corrections of Janecek [J. Phys. Chem. B 129, 6264 (2006)], presented recently by MacDowell and Blas [J. Chem. Phys. 131 074705 (2009)] to account for the intermolecular potential energy of spherical, rigid, and flexible molecular systems, to deal with the contributions to the microscopic components of the pressure tensor due to the dispersive long-range corrections. We have performed Monte Carlo simulations in the canonical ensemble to obtain the interfacial properties of spherical Lennard-Jones molecules with different cutoff distances, $r_c=2.5$, 3, 4, and 5sigma. In addition, we have also considered cutoff distances $r_c=2.5$ and 3sigma in combination with the inhomogeneous long-range corrections proposed in this work. The normal and tangential microscopic components of the pressure tensor are obtained using the mechanical or virial route in combination with the recipe of Irving and Kirkwood, while the macroscopic components are calculated using the Volume Perturbation thermodynamic route proposed by de Miguel and Jackson [J. Chem. Phys. 125 164109 (2006)]. The vapor-liquid interfacial tension is evaluated using three different procedures, the Irving-Kirkwood method, the difference between the macroscopic components of the pressure tensor, and the Test-Area methodology. In addition to the pressure tensor and the surface tension, we also obtain density profiles, coexistence densities, vapor pressure, critical temperature and density, and interfacial thickness as functions of temperature, paying particular attention to the effect of the cutoff distance and the long-range corrections on these properties. According to our results, the main effect of increasing the cutoff distance (at fixed temperature) is to sharpen the vapor-liquid interface, to decrease the vapor pressure, and to increase the width of the biphasic coexistence region. As a result, the interfacial thickness decreases, the width of the tangential microscopic component of the pressure tensor profile increases, and the surface tension increases as the cutoff distance is larger. We have extended the procedure to deal with different mixtures of Lennard-Jones molecules, including asymmetric and symmetric binary mixtures. We have also checked the effect of the impulsive contribution to the pressure due to the discontinuity of the intermolecular interaction potential when it is cut. If this contribution is not accounted for in the calculation of the microscopic components of the pressure tensor, incorrect values of both components as well as a wrong structure along the vapor-liquid interface are obtained.
Viscosity Equations for o-Xylene, m-Xylene and p-Xylene

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O-xylene (o-C6H4(CH3)2), m-xylene (m-C6H4(CH3)2) and p-xylene (p-C6H4(CH3)2) are isomers in structure. They are not only important organic chemical raw materials but also widely used as solvent or synthesizing monomers in many fields, such as chemical industry, paint, medicine and so on. Viscosity is the fundamental thermophysical property of fluids. Within the energy and chemical industry, the viscosity equation over wide range of temperatures and pressures is very important, not only for science but engineering. However, the viscosity equations for o-xylene, m-xylene and p-xylene have not been developed so far. In this work, the available experimental viscosity data were screen sorted through the published literatures and the viscosity equations for o-xylene, m-xylene and p-xylene were developed by the nonlinear fitting algorithm based on the Levenberg-Marquardt algorithm. All the three viscosity equations were expressed as the sum of two parts: the dilute-gas region and the residual region. The viscosity equation for o-xylene (m-xylene, p-xylene) is valid for temperatures from triple point to 400K (650K, 500K) with pressures up to 300MPa (240MPa, 280MPa). The uncertainties of properties calculated with the new equations in viscosity were evaluated reasonably. The behaviors of the equations were also assessed within the region of validity and at higher temperatures and pressures.
A new cubic equation of state and its mixing rules are presented. The corresponding parameters are calculated from the second virial coefficient data of binary mixtures. The methodology to get the equation of state is presented and applied for some hydrocarbon binary mixtures. The resulting phase equilibrium diagram of binary mixtures are compared to experimental data and, also to the results obtained using other cubic equations of state.
Ionic Liquids (ILs) are an exciting class of compounds of high interest from a technological point of view. One of the applications that is raising more interest is their possible use as solvents to carry the conversion of CO₂ into more valuable compounds. Theoretical approaches provide an attractive option to screen ILs properties and give quick answers to guide the experiments, becoming a crucial tool for process design [1]. This work illustrates a practical example based on the solubility of greenhouse and acid gases on the butylmethylimidazolium methylsulfate \([\text{C}_4\text{mim}]\text{[MeSO}_4]\) IL, in order to study its feasibility for gas separation and conversion. A simple but reliable molecular model, within the framework of the soft-SAFT equation of state [2] is presented for the ionic liquid based on structural information and molecular simulations, and coarse-grained models are used to model the different gases. The absorption of relevant gases for the separation/conversion process (CO₂, CH₄, CO, H₂, SO₂, H₂S) in \([\text{C}_4\text{mim}]\text{[MeSO}_4]\) is modeled and compared with experimental data using a minimum amount of binary data. From this information, the ternary diagrams of \([\text{C}_4\text{mim}]\text{[MeSO}_4]\) with CO₂ and the acid gases SO₂ and H₂S are predicted, and the selectivity of CO₂ by respect all the gases is evaluated, with particular attention to the contaminants above mentioned.

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References

The thermal behavior, glass transition temperatures, crystallization, melting temperatures, enthalpies and entropies of isotropization, of ionic liquids (ILs) of the 1-benzyl-3-methylimidazolium family, [BzC1im]+, with five different anions: chlorine; tetrafluoroborate; hexafluorophosphate; 1,1,2,2-tetrafluoroethanesulfonate and bis(trifluoromethylsulfonyl)imide, are presented. Heat capacities of the condensed phases were measured by continuous and step method in the temperature interval from 258 K to 358 K by Tian-Calvet microcalorimeter and, at \( T=298.15 \) K, by the drop calorimeter. By comparison with the CnC1im+ IL series, the obtained results give insights into the anion character and topology and the understanding of the benzyl group contribution to the thermophysical properties of ionic liquids.

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Thermophysical Properties of Benzyl Imidazolium Ionic Liquids

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The thermal behavior, glass transition temperatures, crystallization, melting temperatures, enthalpies and entropies of isotropization, of ionic liquids (ILs) of the 1-benzyl-3-methylimidazolium family, [BzC1im]+, with five different anions: chlorine; tetrafluoroborate; hexafluorophosphate; 1,1,2,2-tetrafluoroethanesulfonate and bis(trifluoromethylsulfonylimide), are presented. Heat capacities of the condensed phases were measured by continuous and step method in the temperature interval from 258 K to 358 K by Tian-Calvet microcalorimeter and, at T=298.15K, by the drop calorimeter. By comparison with the CnC1im+ IL series, the obtained results give insights into the anion character and topology and the understanding of the benzyl group contribution to the thermophysical properties of ionic liquids.

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Thermophysical Properties of Protic Ionic Liquids

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In this work the heat capacity and the vapor pressures by Knudsen effusion as well as, the gaseous phase composition by means of quadrupole mass-spectra analyzer, was used to evaluate the complex equilibrium vapour liquid equilibrium of Protic Ionic Liquids, as 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN) and 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) and a series of carboxylic acids (Propionic, butanoic, isobutanoic acids). The obtained results will be compared, analyzed and discussed concerning the effect of different base/acid compositions on their cohesive energy and volatility and the composition speciation of the PILs with the base/acid ratio and pH.

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Filipe M.S. Ribeiro acknowledges the financial support from FCT and the European Social Fund (ESF) under the Community Support Framework (CSF) for the award of a Research Grant SFRH/BD/94211/2013. Ana S. M. C. Rodrigues acknowledges the financial support from FCT for the award of a research grant with reference SFRH/BD/81261/2011.
This work presents a new equation to calculate the surface tension of silanes. As a first step, a detailed statistical analysis of the data available on the surface tension of silanes was made; also, a factor analysis approach was adopted in order to identify the most significant parameters that influence the surface tension of these compounds. The data were then regressed with the most reliable semi-empirical correlation methods in literature based on the corresponding states theory. The proposed equation is very simple and gives noticeable improvement with respect to similar existing correlations. The same physical parameters considered in the proposed equation were also adopted as input parameters in a multi-layer perceptron neural network, to predict the surface tension of silanes. The multi-layer perceptron proposed has one hidden layer, determined according to the constructive approach. The model developed was trained, validated, and tested for the set of data collected, showing that the accuracy of the neural network model is higher than that of the methods proposed in literature.
A Modified Kardos Equation for the Thermal Conductivity Prediction of Refrigerants

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Back in the 1934, Kardos derived a theoretical equation for the thermal conductivity of liquids starting from the Bridgman equation. He assumed that the temperature drop in the liquid changes exponentially and that the energy drop occurs in the intermolecular spaces. Then he assumed that the heat is transferred along a row of molecules with the velocity of sound. In Kardos equation, thermal conductivity is a function of density of liquid, heat capacity at constant pressure, speed of sound in liquid, average distance between centers of molecules (used by Bridgman), and diameter of molecules. For the average distance between centers of molecule, he assumed a constant value for all liquids while a cubic distribution of molecules was assumed. Even if the Kardos equation has strong theoretical basis and it was considered as a starting point to many other interesting studies, the proposed formula leaded often to very poor results. Thus, this work presents a modification of the Kardos equation specifically oriented to refrigerants. The proposed equation was tested for both liquid and vapor thermal conductivities. Results show that the proposed equation is able to predict the thermal conductivity with very low deviation for the main refrigerants.
Recently, we developed a path-integral method for calculating virial coefficients of flexible molecules, with full inclusion of quantum effects. In this work, we apply the method to calculate second virial coefficients from a recently developed state-of-the-art flexible-monomer pair potential for water. The potential has been fitted to high-quality ab initio calculations at about a quarter million grid points. Because the monomers are flexible rather than fixed at the H$_2$O geometry, the potential can provide a high-accuracy representation not only for H$_2$O but also for D$_2$O. These are the first calculations of the second virial coefficient for these molecules to analyze the influence of both flexibility and quantum effects. We present calculated second virial coefficients for both H$_2$O and D$_2$O between 200 K and 2000 K. Knowledge of uncertainty in the pair potential allows us to make reasonable estimates of the uncertainty in the second virial coefficient. For both H$_2$O and D$_2$O, our results are in reasonable agreement with the available experimental data, but extend to significantly higher and lower temperatures where current knowledge is lacking for these important fluids. The effect of flexibility on the second virial coefficient is found to be smaller than some previous estimates in the literature.
Size-Controlled and Electro-Sterically Stabilized Au Nanoparticles

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This poster describes the gram-scale synthesis of size-controlled hydrophobic gold nanoparticles and a phase transfer for water soluble particles by electro-sterically stability. The hydrophobic gold nanoparticles were generated by via reduction reaction of tetrachloroaurate hydrate as gold precursor in the mixture of 1,2-dichlorobenzene as solvent and oleylamine and oleic acid as surfactant and a mild reducing agent at 190 °C. Size of the hydrophobic Au nanoparticles is possible to a change of 440 % from 10 nm to 54 nm by adjusting volume ratio of the co-surfactant in the synthetic procedure of the particles. The size change in wide range is attributed to high controllability on a particles growth by a surfactant, compared to a reaction temperature and time. When the proportion of oleic acid of the used surfactants increased, Au nanoparticle size was increased by the low binding ability on a growing particle surface. It is a very important to size change of gold nanoparticles in one synthetic system, because optical and thermal properties of gold nanoparticles considerably depend on the size. The as-prepared hydrophobic Au nanoparticles could be transferred into water phase. In detail, the Au particles were dispersed in chloroform and then added to a cetyl trimethylammonium bromide aqueous solution at room temperature. The resultant solution was centrifuged at 3,000 rpm, and the precipitation was washed with ethanol. The hydrophilic AuNPs were well dispersed in water, methanol, and ethanol.
Atmospheric aerosols play a key role in affecting climate, pollution and human health by influencing the properties and lifetimes of clouds and precipitation. There is therefore great motivation to understand the underlying molecular mechanisms involved in the nucleation of liquid droplets. One important quantity in nucleation studies is the excess free energy. In this work, we extract this property using a novel disassembly method (Hoi and Ford [1]) based on the Jarzynski relation [2]. We first investigate clusters of pure water (using the TIP4P/2005 model [3]) followed by sulfuric acid-water clusters since sulfuric acid is a key player in terms of acting as condensation nuclei. Our first study evaluates the free energy of splitting a \(2N\) water cluster into two \(N\) sub-clusters to obtain the curvature-dependent surface tension and the results are compared to other reports in the literature. We then move on to simulating complete disassembly of water clusters to extract the excess free energy curve, which was established to be in good agreement with internally consistent classical theory (ICCT) [4]. Furthermore, the nucleation rate is calculated using the classical Becker-Döring equations and compared to experimental values by Brus et al. [5-6] It was found that our values lie within two orders of magnitude of the experimental data within the range of supersaturation studied at 300 K. Finally, investigations into the excess free energy surface are begun for sulfuric-acid water clusters using a newly developed potential model based on empirical valence band (EVB) theory [7].

References

Porosity in carbon fiber reinforced polymers (CFRP) degrades the engineering performance, especially the interlaminar shear strength. In this work the porosity content of CFRP was successfully determined by thermal diffusion time measurements based on pulsed thermography experiments. The thermal diffusion time is defined as $t_{d} = L(\phi)^2 / \alpha (\phi)$ where $L$ is the sample thickness and $\alpha$ represents the thermal diffusivity. Both parameters depend on the porosity content $\phi$. The sample thickness – porosity relation is explained using a geometrical model for a 1D volume expansion. The effective thermal diffusivity is modeled by using an effective medium theory (EMT), particularly the Maxwell-Garnett Approximation (MGA). For the accurate prediction of the effective thermal diffusivity of porous CFRP, more information about the microstructure is required, because it not only depends on the volume fraction and the material parameters of each phase. Therefore the pore shapes and their distribution are of significant importance. Oblate shaped pores will lead to a decreased thermal diffusivity. In this work the microstructural information is derived from cone-beam X-ray computed tomography (CT) measurements. The effective thermal diffusion time was determined for 116 CFRP test specimens with different porosity contents and different number of plies. The correlation between the effective diffusion time models and the experimental results allows a quantitative evaluation of porosity with pulsed thermography. CT measurements were used to validate the results. The accuracy of porosity evaluation based on thermal diffusion time measurements is comparable to ultrasonic testing.
In recent years, against the background of energy shortage and with the aim of environmental protection, the search for alternative fuels including biodiesel has become an urgent task. For the future application of biodiesel and its mixture, the thermophysical properties, especially the viscosity and interfacial tension are the important index to evaluate its liquidity, lubrication and atomization characteristics, and is of importance to design and optimize the engine injector as well as safety of oil supply. The work intends to carry out the following work. Firstly, with the new developed pendent drop experiment setup, the surface tension of several kinds of biodiesels and their mixtures were measured between 303 K to 363 K. For the complete temperature range, the pendent drop apparatus was firstly checked with water and heptane in the temperature range from 303 K to 363 K. The expanded uncertainties with a confidence level of more than 95 % (k = 2) are estimated to be ±2 % for surface tension. And then, a DFT model will be developed for the calculation of the surface tension of biodiesel and its mixtures.
Deuterium solvent isotope effects on the contribution of proton hopping to molar conductivities at temperatures above 318 K have been determined for the first time. Limiting molar conductivities, $\Lambda^*$, of potassium hydroxide and hydrochloric acid have been measured from $T = 298$ K to $T = 598$ K at $p \sim 20$ MPa in both H$_2$O and D$_2$O, using a unique high-precision flow-through AC electrical conductance instrument. From these results, single ion limiting conductivities, $\lambda^*(H_3O^+), \lambda^*(D_3O^+), \lambda^*(OH^-)$ and $\lambda^*(OD^-)$ have been derived using new single ion values for $\lambda^*(Cl^-)$ reported recently by our group [1]. Walden products ($\lambda^*\eta$) for each ion were found to be simple exponential functions of temperature and solvent density. Walden product ratios for the deuteron/proton and deuteroxide/hydroxide, $(\lambda^*\eta)_{D_2O}/(\lambda^*\eta)_{H_2O}$, showed a clear difference between light and heavy water, with a more efficient transport mechanism in light water over the entire temperature range. The $H_3O^+$ and $OH^-$ ions and their deuterated counterparts are known to move through solution by diffusion through the bulk solvent or through proton hopping. To determine the excess limiting ionic conductivity arising from proton hopping, we have adopted the method used by Tada et al. [2,3] who postulated that the contribution to the experimental conductivities of the hydronium and hydroxide ions from diffusion, $\lambda^*(H_3O^+, \text{diff.})$ and $\lambda^*(OH^-, \text{diff.})$, can be assumed to be the same as those for $K^+$ and $Cl^-$, respectively:

$$\lambda^*(H_3O^+, \text{hopping}) = \lambda^*(H_3O^+, \exp.) - \lambda^*(H_3O^+, \text{diff.}) = \lambda^*(H_3O^+, \exp.) - \lambda^*(K^+, \exp.) \quad (1)$$

$$\lambda^*(OH^-, \text{hopping}) = \lambda^*(OH^-, \exp.) - \lambda^*(OH^-, \text{diff.}) = \lambda^*(OH^-, \exp.) - \lambda^*(Cl^-, \exp.) \quad (2)$$

From 298 to 598 K, ionic transport due to proton hopping was found to be greater for $H_3O^+/D_3O^+$ than for $OH^-/OD^-$. This mechanism became less important as temperature increased.

References

Boric Acid Ionization Constants and Ion-Pair Formation Constants of Sodium and Potassium Borate under Nuclear Reactor Coolant Conditions by AC Conductivity Methods

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Boric acid is used in the primary coolant of pressurized water (PWR) nuclear reactors as a neutron absorber to control the reactor reactivity. Quantitative thermodynamic and transport property databases are needed to model the boron precipitation reactions in fuel deposit crevices, which adversely affect the neutron flux. Here, we report new boric acid ionization constant that have been determined from $T = 548$ K to $T = 623$ K at a constant pressure $p \sim 20$ MPa using a unique high-precision flow-through AC electrical conductance instrument. Frequency-dependent electrical conductivities of aqueous solutions of boric acid, sodium borate and potassium borate have been measured over ionic strengths from $10^{-4}$ to $10^{-1}$ mol·kg$^{-1}$. The concentration-dependent experimental molar conductivities, $\Lambda$, were analyzed with the Turq-Blum-Bernard-Kunz ("TBBK") ionic conductivity model to yield values for the ionization constant of boric acid, $K_{11}$, to an accuracy of ±1 percent at $T = 623$ K. These compare well with extrapolated values from accurate potentiometric measurements at temperatures up to 573 K and steam saturation pressures [1, 2]. The TBBK fits to molar conductivity data for the borate salts yielded statistically significant ionic association constants for the species Na[B(OH)$_4$]$^0$ and K[B(OH)$_4$]$^0$ at $T > 573$ K. These new data are consistent with extrapolations of potentiometric data obtained below 473 K [3]. Our results also confirmed the validity of the new 2006 IAPWS formulation for the ionization constant of water, pH$_{w}$ [4].

References

Hydrate phase equilibria for the binary methane and water mixture were measured by high pressure differential scanning calorimetry in mesoporous and macroporous silica that had controlled pore size ranging from 4 nm to 200 nm. Oscillating dynamic method was used to form hydrates and determine the decomposition conditions of methane hydrates. Significant shifts of dissociation temperature were observed and fitted by Gibbs-Thomson equation. The experimental data up to 50 MPa indicated the interfacial energy in the confined media showed a pressure dependency. The enthalpy of hydrate fusion in confined media were experimentally measured and calculated by Clapeyron equation. Both methods indicated that the enthalpy of fusion was independent of pore size. The effects of interfacial energy on phase equilibria were investigated quantitatively by grafting of silica surface. The dissociation temperatures of methane hydrates in hydrophobic and hydrophilic silica were significantly different. Methane hydrates in strong hydrophobic porous silica tended to behave as bulk methane hydrates in terms of the equilibrium temperature. The measured phase equilibria data, interfacial energy and enthalpy were considered as important parameters for different gas hydrate simulation models.
We have developed a noncontact laser modulation calorimetry to measure heat capacity and thermal conductivity for liquid metals using an electromagnetic levitator under a dc magnetic field [1-4]. A dc magnetic field is applied to suppress surface oscillation, translational motion of the droplet as well as convection in the droplet with the Lorentz force. For measuring heat capacity, convection in the droplet should be remained to promote heat transfer, which provides a quasi-adiabatic condition. In the present study, the heat capacity of liquid cobalt at constant pressure was successfully measured under a lower dc magnetic field of 3 T. On the other hand, convection in the droplet should be minimized to obtain a true thermal conductivity of liquid cobalt. For this purpose, a higher dc magnetic field is required. However, cobalt has a higher magnetic susceptibility even in a liquid state, which generates a magnetic force on liquid cobalt in a magnetic field gradient. This causes unstable levitation, which makes thermal conductivity measurement difficult. In this study, the thermal conductivity of liquid cobalt was measured under dc magnetic fields ranging from 3 to 9 T. The effect of magnetic force on the levitation was quantitatively discussed. Details of experiment, results and discussion will be presented in the symposium.

References

The Kohn-Sham density functional theory (DFT) is a popular approach to compute condensed phase properties. In Kohn-Sham DFT, the local or semi local density functionals do not capture van der Waals interactions accurately. An accurate description of van der Waals interactions is essential in determining thermodynamic properties of molecules. The development of fully non local van der Waals density functional adequately describe dispersion interactions. In this work, we present first principles Monte Carlo simulations to obtain vapor liquid coexistence curves for hydrofluorocarbons by using Becke-Lee-Yang-Parr (BLYP) functional, dispersion corrected functionals, and with rVV10 nonlocal van der Waals density functional.
Effects of Hydrogen Bonding, Viscosity, and Polarity on Heat Transfer Nanofluids Containing Fe$_2$O$_3$ Nanoparticles

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It has been shown that the alignment of Fe$_2$O$_3$ nanoparticles in H$_2$O can enhance the thermal conductivity of nanofluids. To better understand solvent (base fluid) effects such as hydrogen bonding, viscosity, and polarity, nanofluids were prepared by mixing Fe$_2$O$_3$ nanoparticles and various base fluids (H$_2$O, ethanol, 1-propanol, isopropanol, 2-propanone, hexane, cyclohexane, ethylene glycol, glycerol, etc), the dispersions and alignments of the Fe$_2$O$_3$ nanoparticles in these solvents with and without an applied magnetic field were investigated using an optical microscope. The microscope images indicated that inter-molecule hydrogen bonding of the base fluids with one OH group (H$_2$O, ethanol, 1-propanol, isopropanol) could help to disperse and align the Fe$_2$O$_3$ nanoparticles. The intra-molecular hydrogen bonding causes a dramatic increase in viscosity for fluids with multiple OH groups, such as ethylene glycol and glycerol, and makes the dispersion and alignment difficult. Adding water to those fluids could lead significantly reduced viscosity and make the particles disperse and align well. Polarity studies indicated that higher polarity yields better dispersion and alignment of the Fe$_2$O$_3$ nanoparticles. Thermal studies showed that thermal conductivity of nanofluids with hydrogen bonding existed in base fluid is enhanced compared to the theoretically calculated data. Intermolecular hydrogen bonding between water and ethylene glycol increases the thermal conductivity value of nanofluids while decrease the fluid viscosity. As high thermal conductivity enhancement with minimal viscosity increase is the goal of heat transfer nanofluids, the current research may open new door to better understanding fundamental nature of nanofluids.
the
The software developed for calculating the thermodynamic and transport properties for working fluids in energy engineering has been designed for very convenient use by engineers who routinely calculate heat cycles, steam or gas turbines, boilers, heat pumps, or other thermal or refrigeration processes. The following software solutions will be presented: Add-In FluidEXLGraphics for Excel®, Add-On FluidLAB for MATLAB®, Add-On FluidMAT for Mathcad®, Add-On FluidDYM for Dymola® and SimulationX® (Modelica), Add-On FluidVIEW for LabVIEW™, and Add-On FluidEES for the Engineering Equation Solver®. Through the use of the developed program FluidSplines extremely fast spline-based property functions can be provided. For calculating and plotting large-size and camera-ready thermodynamic charts the program FluidDIA was prepared. The International Steam Tables App is available for iPhone, iPad and iPod touch, and for Android smart phones and tablets. Software for calculating properties of water and steam, and other fluids is available for Texas Instruments®, Hewlett Packard®, and Casio® pocket calculators, and is particularly interesting for students. The properties of several working fluids can be calculated online using Zittau’s Fluid Property Calculator at the website www.fluid-property-calculator.com.

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The program libraries for calculating the thermophysical properties for water and steam, for mixtures with water and steam, and for other working fluids are designed for practical use by engineers who calculate heat cycles, steam or gas turbines, boilers, heat pumps, or other thermal or refrigeration processes. They can calculate thermodynamic properties, transport properties, thermodynamic derivatives and inverse functions. The following property libraries are being presented here: LibIF97 for water and steam, LibIF97_META for metastable steam, LibICE for ice, LibSeaWa for seawater, LibHuGas for humid combustion-gas mixtures also at high pressures, LibHuAir for humid air also at high temperatures and pressures, LibAmWa for ammonia/water mixtures in absorption processes and the Kalina process, LibWaLi for water/lithium bromide mixtures in absorption processes, LibIDGAS for combustion gas mixtures, LibIdGasMix for 25 ideal gases and their mixtures, LibRealAir for real dry air, LibCO2 for carbon dioxide including dry ice, LibNH3 for ammonia, LibR134a for the refrigerant R134a, LibPropane for propane, LibButane_Iso and LibButane_n for isobutane and n-butane, LibD4, LibD5, LibD6, LibMDM, LibMD2M, LibMD3M, LibMD4M, and LibMM for siloxanes used as ORC working fluids, LibC2H5OH for ethanol, LibCH3OH for methanol, LibH2 for hydrogen, LibN2 for nitrogen, and LibHe for helium. In addition, property libraries for a number of hydrocarbons are available. These libraries contain the most accurate algorithms currently available for calculating thermodynamic and transport properties. For extremely fast property computations in CFD or non-stationary process modelling, spline-based property libraries are available. The property libraries can be used in user-specific programs written in Fortran, C++, C#, Java, Pascal (Delphi), Python, Visual Basic or other programming languages under the operating systems Windows, Unix/Linux or Mac OS. In addition, add-ons for the use of these property libraries in Excel®, MATLAB®, Mathcad®, Engineering Equation Solver® (EES), Dymola® and SimulationX® (Modelica), and LabVIEW™ are available.
The development and operation of desalination plants require the knowledge of accurate thermodynamic properties of seawater and the ability to calculate them quickly. In 2013, the International Association for the Properties of Water and Steam (IAPWS) adopted the "Advisory Note No. 5: Industrial Calculation of the Thermodynamic Properties of Seawater" (IAPWS 2013) as an international standard for the calculation of the thermodynamic properties of seawater for industrial use. This standard contains an equation of state for the Gibbs free energy for seawater consisting of a part for pure liquid water and a part for dissolved sea salt. The water part is computed from the "IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam" (IAPWS-IF97) and the saline part from the "IAPWS Formulation 2008 for the Thermodynamic Properties of Seawater" (IAPWS-08). The industrial formulation is valid for seawater at temperatures from –12°C to 80°C, pressures from 0.0003 MPa to 100 MPa, and salinities up to 120 g kg⁻¹, with some restrictions in certain regions. All thermodynamic properties and inverse functions can be computed. When using the industrial formulation IAPWS 2013, the uncertainties of the calculated seawater properties are slightly greater than those of the scientific formulation IAPWS-08. The difference results from the use of IAPWS-IF97 in the IAPWS 2013 industrial formulation and the use of the scientific formulation IAPWS-95 in the IAPWS-08 scientific formulation for the pure-water part. The computing speed of the industrial formulation IAPWS 2013 for seawater, however, is increased in the order of 100 to 200 depending on the property function in comparison with the use of the scientific formulation IAPWS-08. The industrial formulation IAPWS 2013 for seawater can be applied in calculations for analyzing, designing, simulating, operating, and optimizing desalination processes and for cooling processes with seawater in power plants.
In fluid mixtures composed of more than three components, diffusive mass transport is driven not only by concentration gradient of the component but also by concentration gradient of other components (cross diffusion) and by temperature gradient (Soret effect). Although it is important to evaluate cross diffusion coefficient and Soret coefficient for understanding mass transport phenomena in fluid mixtures, there has not been an established measurement technique even for ternary systems. In the present study, we have developed the theory for measurement of cross diffusion coefficient and Soret coefficient in ternary fluid mixtures by Soret Forced Rayleigh Scattering (SFRS) method. SFRS is an optical measurement technique using lasers. Using this method, it is expected to realize high speed (less than 10 ms), small sample volume (less than 1 ml) and non-contact measurement for ternary solution. In the measuring principle, two probing lasers having different wavelengths are used. Difference in compositional dependence of refractive index by wavelength causes two different signals. Analyzing two signals in combination, it becomes possible to simultaneously evaluate two main diffusion coefficients, two cross diffusion coefficients and two Soret coefficients of ternary solution. We have constructed apparatus based on SFRS method with two probing lasers of different wavelengths (403 nm and 639 nm). Using this apparatus, we have preliminarily measured diffusion coefficient and Soret coefficient on the ternary mixture with n-dodecane, isobutylbenzene, and 1,2,3,4-tetrahydronaphthalene (equal weight fractions) at 25.0 °C by two probing lasers.
Development of an OPLS-like Force Field for Monte Carlo Simulations of Alicyclic Compounds

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Molecular simulation methods are gradually becoming powerful tools for quantitative description of thermodynamic properties for various systems. Modern computational resources allow Monte Carlo (MC) simulations for complex organic molecules of different classes. The primary goal of the present work is to develop a force field (FF) for MC simulations capable of predicting enthalpies of vaporization and densities of alicyclic compounds. MC simulations were carried out in the NPT-ensemble for liquid and gas boxes at $T = 298.15$ K. Liquid densities and enthalpies of vaporization for the cyclopentane–cyclohexane, cyclopentanone–cyclohexanone, and $\gamma$-butyrolactone–$\delta$-valerolactone pairs were used for optimization of the Lennard-Jones FF parameters. Atomic charges were obtained from quantum-chemical calculations. All other parameters were forwarded from the OPLS-AA-like force field [1]. The parameter optimization was performed with the use of the fractional factorial design. The number of factors and their levels were individually chosen for each numerical experiment and depended on the complexity of a particular functional group appearing in the studied molecule. A bootstrap procedure [1] was used to reduce the number of required simulations. The obtained force field was used for prediction of enthalpy of vaporization and liquid density for homologous series of cycloalkanes, cyclic ketones and lactones. The obtained results were in good agreement with the experimental values.

References

Superposition of a Static Magnetic Field Orthogonal to an Alternating Magnetic Field and the Heating of Ferrofluids for Applications in Hyperthermia

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The current methods for treating cancer are radiation and chemotherapy, which could be complemented by methods for controlled release of drugs in order to reduce side effects. The advantage of the hyperthermia treatment is that the amount of drugs used is lower; its elimination from the body is faster and more economical than chemotherapy. Hyperthermia, also known as thermotherapy is based on heating of nanoparticles by the application of an alternating magnetic field. The increase of the temperature depends on the nature and size of the particles, the carrying fluid, the frequency and size of the applied magnetic field. The heating curves of the sample allow determining the quantity which provides the quantification of a given treatment known as specific absorption rate (SAR). In spite of the studies to analyze the diverse influence heating phenomena during hyperthermia treatments, several basic mechanisms responsible of the heating are not well understood. In particular those related to the structural ordering of the nanoparticles require additional investigation. It is known that magnetic particles can be aligned in a fluid using a constant magnetic field. This alignment can be a determining factor in modifying the thermotherapy effects in a given ferrofluid [1]. In this work, the role of a the alignment of the nanoparticles of a ferrofluid using a constant magnetic field superposed with the usually applied high frequency AC magnetic field is studied in ferrofluids made of 10nm iron nanoparticles in two types of fluids, kerosene and agar and allow us to find their respective SAR.

References

Thermal Conductivity of Ethanol + Rape Oil Mixtures at High Temperatures and High Pressures

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The thermal conductivity of ethanol + rape oil mixtures have been measured with a hot-wire method. The measurements were made in the temperature range from 273 K to 373 K at pressures up to 30 MPa for the concentration from 0 to 100 wt % of ethanol. The total experimental uncertainty of pressure (P), temperature (T), concentration (x), and thermal conductivity (λ) were estimated to be 0.05 %, 15 mK, 0.01 %, and 1.6 %, respectively. To check the accuracy of the method, correct operation of the apparatus, and confirm the reliability of the measured values of thermal conductivity, the measurements were made on pure water, toluene, and air in the temperature range from 273 K to 363 K and at pressures up to 30 MPa. The results for thermal conductivity were compared with more accurate reported data and reference data. In general the agreement between the present thermal conductivity data and majority reported data is within our uncertainty (1.5 % to 2.0 %). The temperature, pressure, and concentration dependences of the mixtures will be discussed. The deviations, Δλ=λ_{exp}(P,T)-xλ_{eth}(P,T)-(1-x)λ_{oil}(P,T), of the measured thermal conductivity data, λ_{exp}(P,T), for the mixtures from the ideal mixtures values calculated using reference data for the pure components were analyzed. The measured thermal conductivity data for ethanol + rape oil mixture were used to develop correlation equation.
I will analyze the dynamics of electrolytes under confinement. I will describe computational and theoretical methods that allow us to understand how the heterogeneous spatial confinement (found in a wide variety of situations such as porous media, or membrane ion channels) can modify qualitatively the dynamics and transport in charged fluids. Understanding the physical mechanisms controlling electrolyte dynamics in such conditions will shade light on their relevance in a wide variety of situations, ranging from nano- and micro-fluidic devices to biological systems. I will show that when particles are suspended in an electrolyte confined between corrugated charged surfaces, electrokinetic flows lead to a new set of phenomena such as particle separation, mixing for low-Reynolds micro- and nano-metric devices and negative mobility.
Monte Carlo Simulations of Two-Phase, Steady-State Flow in Porous Rocks

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The study of two-phase flow in porous rocks is relevant to several fluid flow problems encountered in nature; from the study of diffusion of pollutants in water, to enhanced oil recovery from hydrocarbon reservoirs. Regarding two-phase immiscible flow, not much attention has been given to the steady-state case, in which average flow properties, like the velocity of fluids, remain unchanged [1]. The system under consideration is dissipative, with entropy production due to viscous flow, while all liquid-liquid interfaces are assumed to be in equilibrium. Once the oil-water system has reached steady-state, important relations like the fractional-flow vs saturation can be studied. The aim is to predict the effective and relative permeability of the porous material in addition to finding relations between the macroscopic parameters characterizing the flow: saturation, fractional flow rates, pressure gradients and total flow rates. The standard pore-scale numerical modeling of this problem has been to follow the motion of the fluid interfaces by time integration: one solves the Washburn equation, which is a generalization of the Kirchhoff equation to take capillary pressures due to the interfaces into account [2]. We report evidence that the whole system, under prevalent flow conditions, (flow rate = 50 mm$^3$/sec, dP/dx = 1000 Pa, dT/dx = 0 K), can be regarded to be in local equilibrium. Monte Carlo simulations have been used to evolve samples or sub-parts of the system till the whole system reaches steady-state, the result being independent of the size of the samples of the system above a certain length scale. We find that the system reaches steady state much faster with the Monte Carlo approach, as compared to its evolution using time integration. Besides speeding up the algorithm to a great degree, the thus established equivalence between time averaging and ensemble averaging, enables us to use statistical mechanics to characterize the flow in terms of local flow parameters, like pressure differences and flow composition.

References

Heat of Solution and Solvation of Water and Alcohols in ILs

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In this work the heat of solution at infinite dilution of water, 1-propanol, 1-butanol and 1-pentanol in ionic liquids was measured by Isothermal Titration Calorimetry (ITC). The alkyl chain length effect was explored in the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid series and the cation effect was evaluated by comparison of the solvation in the butyl cation derivatives, butylimidazolium butilpirrolidinium, butilpyridinium and butilpiperidinium. Water and the alcohol series were used as molecular probes to elucidate the differentiation and magnitude of interaction of the –OH groups with the ILs. The trend of the heats of solvation along the alkyl chain length, as well as, the change of the molecular character will be presented and analysed to give insights into the structuration and nanostructuration of the ILs. Analyses of the results obtained by varying both the alcohol’s and the IL’s length allowed us to assess the trend shift in ΔHsol and in ΔHsolv values, and thus on solution interactions along this ILs series, reflecting the discrimination between the polar and non-polar regions of the ILs. It was thus possible to highlight and experimentally support the existence of a Critical Molecular Size (CMS) limit for the nanostructuration, starting at [C6C1im][NTf2], reflecting a change in the molecular structure of the liquid. A very small differentiation of the solvation was found by changing the cation, supporting the model that the solvation of the alcohols involves the interaction of the –OH group with the anion.

Acknowledgements

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Ionic Liquids also have unusual properties derived from its particular structure/nanostructuration and polar and non-polar interactions domains. The electrostatic interactions existing between the cation and the anion have been considered the dominant ones. However, the weak interactions as hydrogen bonds, π–π staking and other non-covalent interaction could be relevant and rule the differentiation between the properties of different families. In this work the heats of solvation of alcohols with different degrees of fluorination in Ionic Liquids by Isothermal Titration Calorimetry is presented. The level of fluorination in tert-butanol: tert-butanol, trifluoro-tert-butanol, hexafluoro-tert-butanol and nonafluoro-tert-butanol was used to give insights into the effect of the increase of alcohol acidity in the –OH to IL interaction. The differentiation of the heats of solvation with the level of fluorination of tert-butanol in different Ionic Liquids will be used for the qualitative and quantitative evaluation of the H-bond interactions between alcohols and ionic liquids.

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Aluminum-based liquid alloys containing one or more transition metals are found to exhibit pronounced negative excess volumes. This effect is investigated in a combined experimental and simulation study on the example of liquid Al-Au. Al-Au received some interest as it played a role in the context of wire bonding between semiconductor devices and conducting surfaces. Here, it is treated as a model system in order to generally study the excess volume on both, a macroscopic and an atomic scale. Density and excess volumes of the liquid pure components, Al and Au, as well as of alloys samples were measured as functions of temperature and composition. These measurements were carried out by electromagnetic levitation using optical dilatometry. In addition, viscosities of the pure components were measured using a high temperature oscillating cup viscometer. Molecular dynamics (MD) simulations were carried out using the LAMMPS package. Existing embedded atom potentials of pure Al and Au were further developed and applied to the liquid pure components. In addition, the two body part of potential is adjusted for the Al-Au interaction using existing excess free energy data. Good quantitative agreement between simulation and experimental data is obtained for all compositions. In particular, the measured negative excess volumes which are larger than 5% of the ideal volume, are reproduced as well the as the experimentally determined thermal volume expansion coefficients. Structural analysis in the MD simulation shows that medium range order emerges in the alloys, accounting for more efficient local packing and a large negative excess volume in this binary system. Furthermore, it is shown that the excess volume cannot be explained by a simple geometric packing argument. In fact, the effective atomic radii become composition dependent contradicting the conventional hard-spheres picture.
Rigid Condensation Polymers Based on Ionic Liquids

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Ionic liquids (ILs) are well known for their tunable structures and it has been proposed that at least $10^6$ "simple" ILs are possible based on readily available starting materials. Here, we extend this concept to the synthesis of vast array of unprecedented polymer materials based on cations linked by rigid groups. Our approach provides opportunities for control over polymer properties (e.g. Tg, free volume) but may also promote supramolecular assembly between polymer chains which can result in highly ordered and porous nanostructures. This talk will focus on material design, synthetic methods, polymer characterizations and modeling.
We describe the development of integrated microfluidic-microelectronic devices to enable the rapid, accurate quantification of physical properties of small volumes of fluids, fluid mixtures, colloids, and suspensions using electronic techniques. We have applied such devices to develop broadband measurements of fluid dielectric properties [1] through the measurement of the complex permittivity function over the broad frequency range from ~100 kHz to 100 GHz, at variable temperatures. We show that such measurements can be sensitive to the ionic conductivity of solutions, and we have applied quantitative models to describe the charge separation effects that occur at electrode-fluid interfaces. We apply these on-chip dielectric spectroscopy techniques to characterize dielectric relaxation in a wide variety of fluid samples, including chemical mixtures, latex bead solutions, and solutions of proteins and DNA. In order to achieve improved sensitivity, we are also applying narrowband electromagnetic techniques, which are used to detect small changes in solution permittivity, and can be used to study dielectric heating effects in microfluidic structures. Together with broadband fluid dielectric measurements, we are also developing microfluidic-based measurements of electron paramagnetic resonance (EPR). Such measurements show good agreement with cavity-based EPR techniques, demonstrating the potential for integration of EPR-based techniques with other on-chip measurements for multi-parameter measurements of a single fluid using microfluidic networks. The potential for integration of different physical property measurements, including thermal properties[2], using electronic measurements combined with microfluidic networks, offers promising new approaches for rapid, high-throughput, accurate characterization of fluid physical properties over a wide range of experimental conditions.

References

Application of PLOT Cryoadsorption Techniques for the Characterization of Trace Components in Natural Gas

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Detailed knowledge about the composition of natural gas is important for many aspects of safe transport and delivery of this product. In this respect even the use of the Extended Natural Gas Analysis will fall short. This is especially problematic and important in ensuring safety through proper gas odorization. In particular, our work focuses on odor masking using detailed analysis of the composition of natural gas both with normal odor and with low odor (geared toward developing an information base of likely odor masking compounds.) To achieve these goals it has been necessary to develop novel sampling techniques that allow for rapid and straightforward determination of trace components in fuel gas. PLOT-cryoadsorption is a dynamic headspace sampling method that was developed at NIST in 2009 for explosives analysis. This method has been expanded by combining multiple PLOT capillary traps into one “bundle.” Multiple traps allows for the rapid collection of large amounts of analyte. After collection, the analytes may be freed by heating and flushing with inert gas. The analytes may then be analyzed by a number of techniques including gas chromatography-mass spectroscopy. These bundles are being developed for both in-line collection processes and rapid cryogenic collection.
Accurate Ptp Data for Argon from Monte Carlo Simulations Using Ab Initio Two-Body and Nonadditive Three-Body Potentials

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Monte Carlo simulations allow for the calculation of accurate thermodynamic properties of a substance provided that the true intermolecular potential energies are known. We have performed Monte Carlo simulations in the isothermal-isobaric ensemble for argon covering a wide range of density along subcritical and supercritical isotherms. We utilized the accurate ab initio potentials of Jäger et al. for the pair interaction energies [1] and the nonadditive three-body contributions [2]. Quantum effects were accounted for by using the quadratic Feynman-Hibbs effective pair potential [3]. Comparison with the best experimental data [4] gives proof to the high accuracy of our results for the gas, liquid, and supercritical phases. We also demonstrate the effects on the results when exchanging the three-body potential for a simple Axilrod-Teller-Muto potential, and what happens when the three-body contributions or the quantum corrections are neglected. We conclude that our approach is able to add accurate values for thermodynamic properties to the available experimental data, especially at extreme temperatures and pressures, and we are confident that it provides the foundation for constructing reliable fundamental equations of state from pure theory for substances where experimental data are difficult to obtain.

References

Experimental Densities of the Thiophene + Octane and Thiophene + Decane Mixtures up to 353 K and 20 MPa

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The thermodynamic properties obtained experimentally are the foundation for obtaining models semi-empirical used to represent and predict the behavior of fluids. The volumetric properties are important in the chemical industry used for the design, simulation and optimization of processes such as distillation, liquid-liquid extraction separation, among others. In addition, knowledge of the density is the basis for the determination of other properties such as solubility and viscosity. To determine the volumetric properties there are different experimental methods which can be broadly divided into direct and indirect. A direct method is developed by W. Wagner which is based on Archimedes' principle of buoyancy. Moreover, one of the indirect methods more used to determine bulk properties of the liquid is developed by Kratky. This method consists in measuring the periods of vibration of a U-shaped tube filled with fluid to study certain pressure and temperature conditions. In this work, experimental densities of two binary mixtures: thiophene (1) + octane (2) and thiophene (1) + decane (3) in the range of 313 to 353 K and up 20 MPa are reported. The two mixtures densities were measured at five different compositions between x= 0 and 1. The measurement system was based on a vibrating tube densimeter (VTD) with a system of data acquisition. The densities of nitrogen and water were taken as calibration fluids for the vibrating tube densimeter.
The use of plasmonic Nanofluids in photothermal applications, such as solar thermal receivers, is a strong subject in current research (see for example the review paper by Mahian et al. in Int. J. of Heat and Mass Transfer, 2013). However, the question about the amount of absorbed energy is of great concern for all of these applications. The calculations are often simplified by neglecting scattering, which in fact becomes important for higher volume fractions, for larger particles or agglomerates. Scattering reduces the absorbed radiation, i.e. usable heat, in the absorber. Thus, in many applications, scattering has to be considered as a loss. In this paper, calculations based on the Mie theory are shown and validated with absorption measurements using an integrating sphere and a UV-Vis Photospectrometer. The calculations show the influence of particle size distributions on the absorption spectra. In order to describe the influence of scattering, besides the absorptions spectra, scattering spectra are calculated and compared with measurement results. Furthermore, the influence of the refractive indices on the absorption behaviour is discussed to show prospects of different materials for solar thermal applications. Using the refractive indices of a medium, the optical behaviour can be predicted. From these calculations, information can be drawn, whether a certain nanofluid can be utilized in absorbers or in applications where high scattering rates are favoured, such as pigments.
One of the attractive features of ionic liquids (ILs) is the ability to vary their thermophysical and transport properties by the choice of cation, anion and substituents. Nonetheless, some general trends have emerged. Particularly, in the search for low viscosity, high conductivity ILs for electrochemical applications, most researchers point to ILs with bis(trifluoromethylsulfonyl)imide ([Tf2N]), bis(fluorosulfonyl)imide ([FSA]) and dicyanamide ([DCA]) anions as good candidates. Lower viscosity ILs generally have higher conductivities. These trends do not hold for a series of cyclic sulfonium ILs that we have synthesized and characterized in our laboratory. Specifically, we have investigated the properties of three ILs with the same cyclic sulfonium cation paired with the [Tf2N] anion, as well as two aprotic heterocyclic anions. All three ILs have attractively low viscosities. In fact, the viscosity of one of the AHA ILs is only 13.5 cP at 25°C. However, the conductivities of the three ILs vary by three orders of magnitude. The conductivity of the [Tf2N] IL at 25°C is 2.56 mS/cm, which is consistent with its low viscosity. By contrast, the conductivities of the two AHA ILs are low, with one of them being just 0.0045 mS/cm at 25°C. Due to both a lower viscosity and lower conductivity, the two AHA ILs deviate significantly from the ideal line on the Walden plot, which implies strong cation-anion association. The CO2 solubility in all three ILs is relatively low, consistent with physical dissolution, even though the two AHA anions readily react with CO2 at low partial pressures of CO2 when paired with tetra-alkylphosphonium cations. We will also report densities and ion diffusivities, as measured by PFG-SE NMR Spectroscopy, of this interesting series of new ILs.
During the last decade in the field of thermophysical and optical quantities of materials, new metrology capabilities have been developed at LNE within the framework of the French National Research Programs and more recently with the support of the European Metrology Research Program. Scientific research has to address more efficiently the needs of the society and also to enabling to increase the industrial competitiveness. According to these challenges, main following key actions have been undertaken [1-3]: - Setting up a new metrological platform (MATIS – MATerials for Industry and Society) dedicated to the characterization of the thermal and optical properties of materials, - Strengthening skills and facilities in the following fields: Radiative properties, Thermal Transport properties... - Developing key initiatives in materials thermal metrology within the framework of the European metrology infrastructure under construction, - Participating and steering the new Task group focused on thermophysical quantities metrology within the framework of BIPM-CCT research activities Scientific research performed by the European metrology institutes on thermophysical quantities of materials should provide more accurate and traceable solutions for enabling new European technology developments dedicated for instance to energy, environment or industrial issues, and also for implementing the scientific knowledge. Therefore, this presentation will mainly focus on research led by the European Metrology Network in the field of thermal metrology of materials applied to some challenging topics (i.e. energy efficiency of power plants...). This regional work will be also compared to other international research actions especially performed within the framework of the BIPM-CCT-TG-ThQ. Acknowledgements: Results of the research work presented in this talk were funded by the French Industry Ministry, the French National Metrology Network and the European Metrology Research Program (EMRP) jointly funded by the EMRP participating countries within EURAMET and the European Union.

References:


Probing Nanoscale Heat Dissipation Away from 1D- and 2D-Confined Heat Sources with Coherent EUV Light

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How is thermal transport affected by spatial confinement in nanoscale systems? The answer to this question is at the forefront of current efforts to build a fundamental understanding of nanoscale thermal transport. While past work has shown that Fourier’s law for heat conduction dramatically over-predicts the rate of heat dissipation from isolated heat sources with dimensions smaller than the mean free path (MFP) of the dominant heat-carrying phonons [1], we have recently demonstrated that heat source size is not the only important dimension to consider [2]. A new regime of nanoscale thermal transport dominates when the separation between nanoscale heat sources is small compared with the dominant phonon MFPs: the collectively-diffusive regime. In this case, close proximity between neighboring heat sources can counteract the reduction in nanoscale heat dissipation from individual sources due to ballistic effects. This finding not only has consequences for thermal management applications and for the fundamental understanding of thermal transport, but also provides a new exciting tool to extract the phonon MFP spectra of materials. In order to probe nanoscale thermal transport, we explore this regime in different sample geometries, in particular heat dissipation away from 1D- and 2D-confined heat sources. We use a pump-probe setup to directly observe the dynamics of periodic arrays of metallic nanostructures (nanolines and nanodots) as small as 20nm and with varying periodicities on dielectric and semiconductor substrates. The structures absorb a 25fs infrared pump pulse; the resulting thermal expansion and relaxation is probed using the diffraction of femtosecond pulses of coherent extreme ultraviolet (EUV) light centered at 30nm, created by tabletop high harmonic generation [3]. Use of such short probe wavelength in an interferometric diffraction measurement allows for an extremely precise contact-less thermometer, sensitive to thermally-generated picometer-scale deformations in the surface profile.

References

The speed of sound and density of a new working fluid, 1-chloro-3,3,3-trifluoropropene (R-1233zd (E)), which is a promising working fluid in the field of low-grade heat recovery, are measured. The measurement was conducted at the temperature from 270 K to 390 K while the pressure up to 5 MPa. Before measurement, the platinum resistance and pressure transducer are calibrated to the accuracy of ±0.05 K and ±1 kPa, respectively. In order to validate the apparatus, the speed of sound and density of R134a was also measured. The results of validation experiment were compared with those calculated from REFPROP. The sonic speed sensor and density sensor has the accuracy of 0.1 m/s and 1 x 10^-4 g/cm^3, respectively. The measurement results will be used in verifying consistency of developed equation of state.
Thermal and optical properties of a liquid resin were studied by thermal lens (TLS), open photoacoustic cell (OPC) and photoacoustic (PA) spectroscopy respectively. In the case of the TLS technique the two mismatched mode experimental configuration was used with a He-Ne laser, as a probe beam and an Ar+ laser the excitation one. The characteristic time constant of the transient thermal lens was obtained by fitting the theoretical expression to the experimental data in order to obtain the thermal diffusivity (D) of the resin. On the other hand, the sample thermal effusivity (e) was obtained by using the OPC technique where the temperature variation of the sample, exposed to modulated radiation, is measured with a photoacoustic sensor. In this technique an Argon laser was used as the excitation source and was operated at 514 nm with an output power of 30 mW. From the obtained thermal diffusivity (D) and thermal effusivity (e) values, the thermal conductivity (k) and specific heat capacity per unit volume (pc) of resin were calculated through of the relationships \( k = e(D)^{1/2} \) and \( pc = e/(D)^{1/2} \). The obtained thermal parameters were compared with the thermal parameters of literature. To our knowledge the thermal characterization of resin has not been reported until now. Our work has applications in laser stereolithography to manufacture 3D printing pieces.
Several experimental techniques reported in the new millennium have enabled the probing of thermal transport in nanoscale and low-dimensional structures. However, the inability of separating the contact thermal resistance has often prevented these techniques from revealing intrinsic size-dependent thermal transport properties. Here we report a novel four-probe measurement method that can obtain both the intrinsic thermal conductance and the contact thermal resistance of individual nanostructures. In this method, the nanostructure sample is transferred across four suspended Pt/SiNx resistance thermometer lines of a microfabricated measurement device. During the measurement, the average temperature rise in the four lines are measured when one of the four lines are electrically heated. By using each of the four lines as the heater lines, a total of sixteen temperature measurements are made. The sixteen temperature measurements can be used to obtain nine thermal resistances in the system. Because the heat flows across the two contacts and the suspended portion of the middle segment of the sample are different and depend on which of the four lines are used in the heater line, the contact thermal resistance and intrinsic sample thermal resistance of the middle segment can be determined. In this work, two samples of patterned Si nanorod with different width have been measured to demonstrate the effectiveness of the method. Because of the ability to obtain both the contact thermal resistance and intrinsic thermal conductance of nanostructure, this new four-probe thermal transport measurement method for nanostructured materials can potentially enable the discovery of a number of unique size-dependent thermal transport phenomena that have or have not been predicted by existing theoretical studies.
Measurements of Infrared Radiative Properties of Crystal Materials at High Temperatures

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The radiative properties of semi-transparent crystal materials are important physical parameters in applications. Zinc sulfide crystal material, which has the advantages of high mechanical strength, high hardness, erosion resistant, and excellent optical transmission from the visible to infrared wavelengths, is the investigated semi-transparent material in this paper. A measurement method was established to determine the optical constants of high-temperature semi-transparent materials in the infrared spectra based on the measurements of apparent spectral radiative properties at different angles and background source conditions. Based on the analysis of radiative transfer, the inverse accuracy for the optical constants using the Levenberg-Marquardt algorithm was numerically verified to give the optimized measurement conditions of apparent radiative properties. The experimental apparatus measuring the apparent radiative properties of semi-transparent materials was established using a FTIR spectrometer, a heating cavity and a standard high-temperature source. High-temperature experiments with ZnS sample were used to experimentally verify the method. The inverse solution results agree well with reported data in the literature. This research works provides a reference for measurements of high-temperature radiation properties of semi-transparent materials in multi-layer structure.
Temperature Measurements Using Multicolor Pyrometry in Thermal Radiation Heating Environments

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Accurate temperature measurements are needed for thermal-structural stress analyses in thermal radiation environments. This paper describes the use of multicolor pyrometry for the measurements of diffuse surfaces in thermal radiation environments that eliminates the effects of background radiation reflections and unknown emissivities based on a least-squares algorithm. A multicolor pyrometer with a near-infrared spectral response of (1100 nm ~ 2400 nm) was used for the measurements after the calibrations of the wavelength, nonlinear intensity and spectral response curves. The temperature of a graphite sample irradiated by quartz lamps was then measured during heating and cooling using the least-squares algorithm based on the calibrated irradiation data. The experiments show that higher temperatures and longer wavelengths are more suitable for the thermal measurements in the quartz lamp radiation heating system. This analysis provides a valuable method for temperature measurements of diffuse surfaces in thermal radiation environments.
The interest on CO₂ hydrates characterization has increased remarkably over the last few years due to the possibility of using them for waste CO₂ recovery, capture and storage. The feasibility of replacing CH₄ by CO₂ in hydrate deposits existing in nature has been discussed, and seems to be a promising alternative with evident environmental benefits in the near future. Nevertheless, the modelling of CO₂ or mixed hydrates has received less attention so far, and the theoretical estimation of their phase equilibria and thermophysical and transport properties still needs further contributions. In this case, rigid non polarizable molecular models have been used to describe H₂O and CO₂, and the three phase CO₂ Hydrate-Liquid H₂O-Liquid CO₂ equilibrium line has been determined using Molecular Dynamics and the direct coexistence technique. The influence of the initial occupancy rate of the different cells of the type I hydrate has been evaluated, as well as the effect of the different parameterizations of the molecular models in each case. It has been found that, although correct qualitative results are found for this type of models up to high pressures, the H₂O model version plays a key role in the precise determination of the phase boundary location, which is by far less sensitive to the CO₂ model version employed.
Transport Diffusivity in Nanoporous Graphene

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With the advent of large-scale fabrication of nanostructured carbon such as graphene and carbon nanotubes has come increased interest in the potential of these structures for use as membrane materials. Recent reports suggest that such structures are selective to the permeation of water molecules in particular[1,2]. It has been proposed that this property may endow nanoporous graphene and graphene sheets as candidates for desalination membranes. The process of diffusion through such membranes is expected to be mediated by adsorption mechanisms and confinement effects at the nanoscale. Computer simulation is an ideal tool for detailed study of the microscopic mechanism of diffusion in such systems. In this work we use steady-state Non-Equilibrium Molecular Dynamics simulations to study the diffusion of water through nanoporous graphene and layered functionalised graphene sheets. This method allows us to systematically investigate the selectivity of these materials and effectively evaluate their potential as reverse osmosis membranes.

References

Liquefied Natural Gas (LNG) is a significant contributor towards meeting the continuously mounting global demand for energy. According to Exxon Mobil Corporation [1], the global demand for LNG is projected to rise by 65% within the next three decades despite the slow demand growth within the last year [2]. This demand is primarily due to the expansion of China, who has become extremely influential in world energy markets due to their ongoing expansion and subsequent increasing energy demand [3]. Consequently, flow assurance within LNG processing facilities has become a major technical and economic issue. The avoidance or remediation of the formation and subsequent deposition of long-chain hydrocarbon (C6+) solids is one key aspect of flow assurance. Under the cryogenic temperatures and high pressures at which LNG processing facilities operate, these hydrocarbons can precipitate out of the LNG and accumulate in the process equipment causing blockages. The ability to predict solids deposition rates depends on many factors, one of which is currently being examined in this work: the thermodynamic equilibrium between LNG and hydrocarbon solids. A commercial differential scanning calorimeter (DSC) was used to determine the melting temperatures for hydrocarbon mixtures containing components analogous to those that precipitate in LNG processing. This apparatus is capable of attaining temperatures as low as 77 K and pressures up to 6 MPa thereby simulating the industrial operating conditions at which precipitation occurs. Melting temperature measurements of LNG analogues under both ambient and plant operating conditions will be presented, together with an analysis of the impact of both solute and solvent composition.

References

Temperature Dependence of Dc Conductivity of Kaolinitic and Illitic Clay

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DC conductivities of illitic (IC) and kaolinitic (KC) clays were measured in the temperature range of 20 °C – 1100 °C. During heating several processes take place in IC and KC – the liberation of physically bound water, dehydroxylation and creation of spinel and mullite. These processes were checked by means of thermogravimetry, thermodilatometry and thermoconductometry. At low temperatures (20 – 350 °C), due to the release and decomposition of physically bound water, H+ and OH− ions are dominant charge carriers in IC and KC. The liberation of physically bound water from the clays takes place in 3 steps in IC, and only in 1 step in KC. After completion of liberation of physically bound water, up to the start of dehydroxylation at the temperature of ~450 °C, the DC conductivity is dominated by a transport of Na+ and K+ ions. During dehydroxylation, H+ and OH− ions, which are released from kaolinite and illite lattices, contribute to the DC conductivity. After a completion of the dehydroxylation, the charge carriers are Na+ and K+ ions. At ~950 °C, small peak of DC conductivity indicates the reconstruction of the metakaolinite lattice into the spinel lattice. In IC, influence of the DC conductivity of the glassy phase (~40 wt.% at 950 °C) suppresses a DC conductivity demonstration of the metaillite * spinel transformation.
Cloud point, tcl, is the temperature at which a homogeneous aqueous solution of a water-soluble amphiphile becomes turbid. Cloud point usually decreases as salinity increases. In this work a study on the cloud point phenomena in aqueous solutions of seven imidazolium-type compounds is presented. These compounds were synthesized in our laboratory and are intended to act as Low Dosage Kinetic Hydrate Inhibitors (KHIs). Knowing the cloud point of a KHI is important for preventing its possible precipitation when injected into hot well streams. Cloud points were visually determined by observing the temperature at which the first sign of appreciable turbidity in the aqueous solution appeared. The effect of several parameters (including concentration of the studied compounds [0.05 to 1.0 g/100 g] as well as type and concentration of electrolytes) on the cloud points was investigated. Some of the studied compounds were compatible (tcl > 60 °C) with very high salinity brines (total dissolved solids > 250,000 mg/kg). Additional experiments carried out in our laboratory indicate that these compounds also showed promising activity as KHIs for natural gas type-II hydrates with large subcooling.
In this paper photothermal radiometry (PTR) and photoacoustic (PA) spectroscopy techniques along with a thermal waves propagation model for a layered system [1], have been used to determine the thermal emissivity of a commercial selective coating (TiNOX) [2] deposited on aluminum and copper foils. PA measurements were made using a modified conventional Rosencwaig cell in which the sample closes the cell on one side and on the other by a transparent window, through which the coating is illuminated by the modulated laser beam at 808nm and with a spot of 5mm. The temperature variations in the air inside the PA cell were detected using an electret microphone coupled to the cell [3]. The PTR system consists of a modulated laser, at 808nm and with a spot of 5mm that impinges directly on the coating, as a consequence the samples heats periodically and the radiation emitted is collected by a couple of parabolic mirrors and sent into a HgCdTe sensor. Both PA and PTR measurements were performed in the range from 5 to 2000Hz. The PA (PTR) signal was normalized with respect to the PA (PTR) signal of the respective substrate. Given that the substrate is very thick compared with the selective coating layers, using the 1-D model for describing the thermal wave (TW) generation on sample surface and its subsequent propagation, it is shown that the normalized PA and PTR signals do not depend on the thermal properties of the layers, but only on the optical and in the light into heat efficiency. Based on this method, and using both the PA and PTR normalized signals, it is shown that the emissivity of the selective coating can be obtained [4]. It is also shown that this procedure can also provide the thermal emissivity for temperatures above room conditions and up to 60°C. In this case the sample is maintained at constant temperature using a controlled Peltier cell.

References

Relative Optical-To-Thermal Energy Conversion Efficiency of NiO/Ni and TiNOX Selective Coatings Measured by Photoacoustic Spectroscopy

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Thermal and optical characterization of materials used in renewable energy industry is a primary need. Photothermal techniques are especially suited to perform such studies, since sample properties can be determined directly from the obtained signals [1]. In thermal solar collectors, an important selective coating property is the efficiency of the coating to convert the incident radiation into heat. This quantity is involved in all the photothermal process and in principle be obtained using the well-known photothermal techniques. In this paper a method to measure this efficiency in selective coatings is presented. The method consists in performing PA measurements using a modified conventional Rosencwaig cell in which the sample closes the cell on one side, and on the other by a transparent window, through which the coating is illuminated by a modulated laser beam from 5 to 2000 Hz. The temperature variations in the air inside the PA cell were detected using an electret microphone coupled to the cell. The efficiency was measured using several wavelengths in the visible up to the near infrared in NiO/Ni and TiNOX selective coatings on aluminum, copper and steel substrates. Interpretation of the experimental data was performed using a one-dimensional thermal wave propagation model approach for a layered system [2,3].

References

Cork stopper is still the most used stopper to seal wine bottles and to preserve wine during storage. During post-bottling aging, oxygen transfer through the stopper occurs and can lead to oxidation reactions. When in excess, a final result of such reactions is color change (browning) and off-flavor appearance, which modify the organoleptic properties of wine. Therefore, it is important to understand how the transport of gases, particularly oxygen, occurs through them. Up to now, the limiting step of gas transfer through cork was not clearly determined. Performing permeation experiments at different pressures we concluded that the limiting step of oxygen transport through cork follows a Fickian mechanism [1] with two different diffusion regimes. We could also investigate the heterogeneity of the diffusion data for different cork stopper [2] and relate it to the heterogeneous internal structure of the cork [3].

References


Partial Molar Enthalpy from Fluctuations at Small Scale

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Experimentally one of the most important quantities to measure during a transformation is the heat of transformation, which can be done directly in calorimeters. From a thermodynamic point of view, this heat can be calculated from the knowledge of partial molar enthalpies for constant pressure transformations or from the partial internal energy for transformations at constant volume. Despite the large interest in these quantities, their calculations from molecular simulations is still a challenge in particular for high density systems, cumbersome molecules, traces or for reacting systems. In the presentation it will be shown how looking at mass and energy fluctuations at small scales in open systems under equilibrium conditions gives a direct access to partial molar enthalpies [1]. This new method, called the small system method, will be applied to molecular dynamics simulations of a reacting system H2=2H at different temperatures for which the calculated heats of reaction agree with experimental data [2].

References

Molecular Simulations Predictions of Thermophysical and Transport Property of Ionic Liquid- Ionic Liquid Mixtures

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In the last decade or so, molecular simulation methodologies have enabled thermophysical and transport property predictions of a large number of ionic liquids and their mixtures. In addition, a number of researchers have predicted phase equilibria of ionic liquids with gases and solvents in order to assess the feasibility of employing ionic liquids as gas separation agents. Such simulations have focused primarily on systems containing only one ionic liquid. Given that ionic liquid-ionic liquid mixtures can greatly expand the range of nonaqueous systems, there is a critical need in determining properties of such mixtures. In this talk, we will describe our initial efforts in addressing this gap in the knowledge. We will report molecular simulation predictions of thermophysical, transport and structural properties of mixtures of ionic liquids based on imidazolium and pyridinium moieties.
Carbon dioxide capture and storage (CCS) is currently considered as a promising option of mitigation actions for stabilization of atmospheric greenhouse gas concentrations. The thermodynamic properties of CO₂-rich streams are particularly important and indispensable for optimum design of pipeline transportation from the point of carbon capture to the storage site. In this work accurate pressure-density-temperature data for binary mixture of carbon dioxide with argon (the molar fraction of CO₂ was greater than 85%) were obtained using the Burnett-isochoric coupling method for temperatures between 293 K and 393 K and pressures between 1 MPa and 12 MPa. The experimental measurement uncertainties were estimated to be within ±5 mK for temperature and ±0.7 kPa for pressure.
Measurement of Surface Tension of Cu-5Sn-1Zn by an Oscillating Drop Technique

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The oscillating drop technique, a well-established method to measure the surface tension of metallic materials, is used in combination with an electromagnetic levitation device to measure the surface tension of liquid Cu-5Sn-1Zn in the temperature range from the liquidus point up to 1700 K. An electromagnetic levitation device employs an inhomogeneous radio-frequency electromagnetic field inside a levitation coil to heat and position metallic specimens. Induced eddy currents are used to heat the material to the liquid phase and exert a Lorentz force, pushing it towards regions of lower field strength. The oscillation of the levitating specimen is monitored by a high-speed camera with up to 600 fps; the temperature of the specimen is measured by a fast pyrometer operating in the near infrared. As electromagnetic levitation is a container-less and contactless method, the contamination of specimens during measurement is dramatically reduced. Furthermore, the investigation of significantly undercooled liquid metals is possible. Results of measurements of surface tension as a function of temperature of Cu-5Sn-1Zn are presented.

Acknowledgements

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1-Propanol (C₃H₇OH) is saturated monohydric alcohol in structure. It can be used as solvent in paint and cosmetic industry. It also is a basic organic reagent to synthesize propylamine applied to produce medicine and agricultural chemical, feed additives, synthetic perfumes and so on. Recently, alcohols have attracted more and more attention as gasoline additives to reduce the formation of soot in combustion and cosolvent in the mixture with CO₂ because of the high solubility of CO₂ in them. However, there is no special equation of state for the thermodynamic properties of 1-propanol so far. In this work, on the basis of thermodynamic properties data from the literatures, a special Helmholtz Equation of State for 1-propanol was developed by the nonlinear fitting algorithm based on the Levenberg-Marquardt algorithm. It is explicit in Helmholtz energy with independent variables of temperature and density. The Equation of State is valid from the triple point temperature to 570K, for pressures up to 208MPa and for densities up to 17mol/dm³. The estimated uncertainties of properties calculated with the new equation in density, vapor pressure, saturated liquid density, saturated vapor density, and the properties with energy were evaluated. The behaviors of the equation of state were also assessed within the region of validity and at higher temperatures and pressures.
In this work we present a method to analyze pulse thermography data, obtained by measurements as well as simulations, to estimate the following three important thermophysical sample parameters: $\omega_0$ (the characteristic frequency, which corresponds to the diffusion time $t_d$), $B_1$ (the Biot number at the front side) and $H$ (the ratio of the Biot number at the rear side $B_2$ to $B_1$). The procedure is referred as Parameter Reconstruction in Frequency and Time Domain (PRFTD) and is a further development of the previous work Parameter Reconstruction in Frequency Domain (PRFD). The procedure was developed for a 1D solid of length $L$. The PRFTD procedure consists of three main steps in time domain with a subsequent fitting procedure in frequency domain. This procedure can be applied for measurements in reflection and transmission mode setup. The three main steps in time domain are:

1) Fit of the measured or simulated data based on physically piecewise continuous trial functions.

2) Estimation of the diffusion time $t_d$ by using the Thermographic Signal Recognition (TSR) method when analyzing reflection mode data or by using the Linear Diffusivity Fit (LDF) method when analyzing transmission mode data.

3) Integral Fourier Transformation (IFT) of the trial functions. The advantages of the IFT are, on the one hand the avoidance of the well-known problems arising from discrete Fourier transformation and on the other hand the applicability of the existing analytical solution of the heat transfer equation in a closed form on the transformed data. Therefore, the remaining material parameters $B_2$ and $H$ can be estimated by a subsequent fitting procedure in frequency domain.

To use the PRFTD procedure only the condition of a homogeneous material must be fulfilled. Due to this characteristic, the PRFTD procedure can be used as a reference method for the calibration of other methods (e.g. TSR and LDF).
Using EUV Photoacoustics for Nanometrology of Ultrathin Films

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Inventive material development and device design require reliable characterization tools to understand the benefits and drawbacks of new nanomanufacturing ideas. In the semiconductor industry in particular, Moore’s Law scaling has pushed the frontiers of nanofabrication so far that the thinnest films and smallest nanostructures being made today cannot easily be measured using current metrology techniques. To overcome these limitations, we implement a non-destructive photoacoustic technique that uses coherent extreme ultraviolet (EUV) light and nanoscale acoustic waves to probe the material properties of nanostructured systems on extremely short length scales. We excite periodic metallic nano-gratings on the surface of low-k dielectric thin films with a femtosecond 800nm laser pump pulse to launch acoustic waves: longitudinal waves (LAWs) within the nanostructures, LAWs traveling down into the film and transverse surface acoustic waves (SAWs) with a wavelength set by the grating period. Because SAWs penetrate only as deep as a fraction of their wavelength, their sensitivity can be isolated to ~10nm films by shrinking their wavelength with shorter grating periods. Wave dynamics are monitored by diffracting 30nm EUV probe light from the surface. Such short wavelength light obtained via tabletop high harmonic generation offers exceptional sensitivity down to picometer surface displacements caused by the nanoscale acoustic waves. Previously we used this technique to characterize a series of 50-100nm thin dielectric films, demonstrating selective sensitivity to the film properties without contribution from the substrate beneath. Here we extend that work to sub-50nm thin film samples where we begin to address how thickness alone may affect the nanoscale elastic properties of a material. Also, we examine softer, highly hydrogenated SiC:H films in which we can explore important trends or thresholds in the relationship between Poisson’s ratio and the decreasing bond coordination that contributes to film softness.
Hydrofluoroolefins (HFOs) have been taken for account as candidates of next generation refrigerant due to their lower GWP compared with HFC refrigerants. In order to replace the alternative refrigerants, accurate physical properties are essential for design the refrigeration/air-conditioning or high-temperature heat pump system. There are, however, very limited experimental data of the transport properties compared with the thermodynamic properties. In the present study, thermal conductivity and viscosity of low-GWP refrigerants are measured in wide ranges with a transient hot-wire method and a tandem capillary tubes method, respectively. In the measuring the thermal conductivities, short (60mm) and long (120mm) platinum wires with diameter of 0.015 mm were used as the line heat source in order to eliminate the contact resistance of the wire ends. The viscosities are obtained by measuring the pressure drops flowing test fluid under laminar flow condition inside two different length capillary tubes (50 and 100 mm) with same diameter connected in series to eliminate the pressure drop at both inlet and outlet of the tubes. This study also deals with development of correlation of the thermal conductivity and the viscosity based on the experimental data using an extended corresponding states (ECS) model. The results show that there are good agreement between the predictions and the present measurements.
Ethane is an important fluid with many applications. It occurs as a secondary component in natural gas or as a byproduct in petroleum refining and is used as basic component for ethylene production. Moreover, it is often employed as a reference fluid in thermophysical property research to develop equation of state models or to validate models for intermolecular forces, which are applied in molecular simulations. Therefore, the precise knowledge of the thermodynamic properties of ethane is desirable. There are several data sets for the speed of sound in ethane reported in the literature, but these data cover only parts of the technically interesting fluid region of the phase diagram. Especially at high pressures above 35 MPa and temperatures above 325 K the speed of sound has not been measured before. It is the aim of this work to fill this gap. Thus, the speed of sound in liquid and supercritical ethane was measured with a double-path-length pulse-echo technique. Measurements were taken on ten isotherms in the temperature range between 240 K and 420 K with pressures up to 100 MPa. The measurement uncertainties are estimated to be 3 mK for temperature, 0.005 % for pressure, and 0.03 % for speed of sound. The purity of the ethane sample was verified by analysis with a gas chromatograph. Comparisons with literature data and equation of state models demonstrate the high accuracy of our measurements. The new speed of sound data are represented by a correlation function, whose functional form was found by the method of structural optimization.
Using Molecular Simulation to Understand the Bulk and Interfacial Behavior of Ionic Liquids

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Understanding the bulk and interfacial properties of room temperature ionic liquids (RTILs) is important for several industrial applications of these fluids. In this presentation, we discuss recent progress in the use of Monte Carlo simulation to better understand the phase and interfacial properties of ionic fluids. We first present liquid-vapor saturation properties of the homologous series 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Cn mim][NTf2]) at temperatures ranging from room temperature to the critical region. We also relate the trends observed in these properties to the microstructure of the saturated liquid and vapor phase. We present results for the homologous series with n ranging from 2 to 12. The calculated properties include saturated liquid and vapor densities, vapor pressures, enthalpies and entropies of vaporization. We also show how the liquid phase microstructure, especially the nano-domains observed for some of these fluids, evolve over the temperature range investigated. In many cases, simulation results are compared to experimental data. We next examine the role of dispersion and electrostatic interactions in the wetting behavior of ionic liquids on non-ionic solid substrates. We study simple models of ionic liquids comprising of spherical cations and anions with variable strengths of electrostatic interactions relative to dispersion interactions. The range of relative ionic strengths that we investigate includes those observed in RTILs and molten alkali halides. Results are presented to show the dependence of contact angle on temperature and substrate strength for fluids with different relative ionic strengths. For all of the fluids studied, we observe a relatively narrow range of substrate-fluid interaction strengths wherein the contact angle is nearly independent of temperature. We discuss now this observation is related to the microstructure of the fluid at the liquid-vapor and solid-liquid interfaces.
The Complex Structure of Ionic Liquids Probed by Molecular Dynamics Simulation

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The concept that the structure of ionic liquids is complex and can exhibit nano-scale segregation started to be investigated almost ten years ago via molecular modeling. A systematic molecular dynamics study has been performed in order to extend the analysis of the mesoscopic segregation behavior observed in different ionic liquids. The analyses include the discussion of the structure factors, $S(q)$, in the low-$q$ range ($1.6 \leq q \text{ nm}^{-1} \leq 2.0$); the confirmation of the periodicity of the polar network of the ionic liquid and its relation to the so-called intermediate peaks; and the characterization of the polar network and the nonpolar regions that are formed along the series using aggregate analyses by means of five different statistical tools. The analyses confirmed that the percolation of the nonpolar regions into a continuous domain can occur but that this is not a sufficient condition for the emergence of a distinct and intense prepeak. The lowest-$q$ peaks of the structure factor spectra (prepeaks) can be assigned to characteristic separations between strands of the ionic liquid polar network that are mediated by nonpolar regions. On the other hand, the second lowest-$q$ peaks reflect the medium-range ordering of the polar network itself. Finally, the systematic comparison between different groups of ionic liquids allows us to rationalize the relative amplitude and position of those peaks with the underlying structure of the ionic liquid and interpret such an outcome in terms of the relative size and nature of the corresponding ions.
Measurements of Thermophysical Properties for HCFO-1233zd(E)

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Power generation systems using organic compounds with low boiling temperatures as working fluid (organic Rankine cycle) is one possible solution to utilize low-grade waste heat. Although HFC-245fa has been popular working fluid for organic Rankine cycles, it has a large value of GWP (Global Warming Potential). Recently produced refrigerant HCFO-1233zd(E) is expected as an alternative for HFC-245fa. At this time, however, available experimental data of this new refrigerant is very limited. In this work, measurements of thermophysical properties for HCFO-1233zd(E) are conducted using three different apparatuses to cover wide range of temperature and pressure. The first apparatus has two constant volume cells with a pressure sensor on the basis of the extracted method to measure vapor pressures and saturated densities in the temperatures from 300 K to 400 K. The second apparatus has a constant volume cell designed for operating at high temperatures and high pressures on the basis of the isochoric method to measure PVT properties in the temperatures from 323 K to 523 K and pressures up to 10 MPa, including the critical region. The final apparatus is based on a metal bellows method to measure densities of the compressed liquid. Vapor pressures, saturated liquid and vapor densities, and PVT properties covering the critical region are obtained from the apparatuses. Based on the present data, correlations for the properties are formulated. In addition, the critical parameters, normal boiling temperature, acentric factor, and heat of vaporization are derived from the present data, and the validity of these properties are also discussed.
Acoustic Gas Thermometers (AGTs) play the major role in measuring thermodynamic temperature through accurate measurements of speeds of sound for dilute gases. The AGT of fixed-path-length cylindrical resonator is an important branch of AGTs. It has shown some preference characteristics in accurate measurements of speeds of sound of dilute gases. Nevertheless, the inconsistency among different modes is the dominant drawback of such AGTs. We made a new oxygen-free copper cylindrical resonant cavity that was machined with the high-precision diamond-turning procedure. The performance of the AGT with the new cavity was assessed through measurements of three non-degenerate longitudinal modes at 273.16 K. The equal and non-equal spaced frequency interval were applied for the scanning of resonant profiles. The corrections of perturbations have been implemented to extract the unperturbed resonant frequencies. The surface fitting for the acoustic virial relation has been made over experimental data in the pressure range from 100 kPa to 550 kPa. The first virial coefficients yielded, such the square speeds of sound at the ideal gas state, agree in the fractional differences of smaller than two parts per million. The new measurements turn out an improvement with the comparison of the previous experimental data obtained by the authors. The new progress is helpful for application of AGT in fixed–path–length for accurate measurement of thermodynamic temperature in large range.
Measurements of the Density, Speed of Sound, Viscosity and Derived Thermodynamic Properties of Geothermal Fluids from South Russia Geothermal Field

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The geothermal fluid samples for the present study comes from geothermal wells Izberbash No.68, No.129 and Ternair No. 27T, No. 38T (Dagestan, south Russia Geothermal Field). The Geothermal Field is located in the southern part of Russia, approximately 60 miles to the south-west of capital city Makhachkala of Dagestan, near Caspian seashore (about 2 mile away from the seashore). The wellhead temperature is within (62 to 69) °C, while the wellhead pressure is within from (0.8 to 2.0) atm. The density, speed of sound, and viscosity of four natural geothermal fluid samples have been measured with Anton Paar Instruments: vibrating-tube densimeters (DMA 4500); sound-speed analyzer (DSA 5000 M); and Schtanbergviscodensimeter (SVM3000), respectively. Measurements were performed at temperatures from (278 to 343) K and at atmospheric pressure. The combined expanded uncertainty of the density, viscosity, and speed of sound measurements at the 95 % confidence level with a coverage factor of \( k = 2 \) is estimated to be- density: 0.0005 % (for DMA 4500 densimeter), 0.02 % or 0.5 kg·m\(^{-3}\) (for the SVM 3000 viscodensimeter) and 0.01 % (for the DSA 5000 M sound-speed analyzer); viscosity-0.35 % (for SVM 3000); and speed of sound-0.1 % (DSA 5000 M), respectively. Measured values of density and speed of sound were used to calculate other very important derived thermodynamic properties of the geothermal fluid samples. Measured values of density, viscosity, and speed of sound were used to develop correlation models which reproduced the experimental data within 0.03 % (density), 2.55 % (viscosity), and 0.06 % (speed of sound), respectively. The measured properties at atmospheric pressure have been used as a reference values for prediction high pressure properties. The temperature behavior of the density, speed of sound, and viscosity for geothermal fluids are just like pure water and other binary aqueous salt solutions. The measured density, speed of sound, and viscosity data were used to develop correlation model (Riedel model) to predict the values of these properties for various concentrations of ions and temperatures from (278 to 343) K. The contribution basic ions in the geothermal fluids (Na\(^+\), Ca\(^2+\), Mg\(^2+\), K\(^+\)) to the total experimentally observed values of the density, viscosity, and speed of sound was estimated.
We describe a novel instrument designed for the indirect measurement of emittance of materials in a variety of aggregate states including solid, powder and liquid forms undergoing processing over a range of temperatures up to and beyond the melting point. The instrument is used to perform hemispherical-directional reflectance factor measurements, from which the emittance can be derived from Helmholtz reciprocity, Kirchhoff’s law and energy conservation. The instrument consists of the following elements: 1) a hemisphere coated with a near-Lambertian diffuser, 2) a high reflectance specular baseplate containing a sample port located at its center, 3) a ring of light-sources around the circumference of hemisphere base, consisting of light-fiber-fed transmissive diffusers and providing illumination to the hemisphere and indirect uniform illumination of the sample, and 4) a viewing port near the center of the hemisphere for receiving reflected light from the sample or reference. The combination of a diffuse hemisphere and high reflectance specular base provides an environment equivalent to that of an integrating sphere for these reflectance measurements. The light-fibers are fed with laser sources and measurements of the reflected light are made with filter radiometers or spectrometers. The reflectometer has been designed to operate within the chamber of a testbed for the study of additive manufacturing processes. It will be used in a facility under development named AMMT-TEMPS (Additive Manufacturing Metrology Testbed - Temperature and Emittance of Melts, Powders and Solids). A primary goal of this facility is the characterization of emittance of materials undergoing laser heating of the additive manufacturing process, enabling accurate determination of true surface temperature of the materials and providing data for modeling of the processes. Preliminary test results of the constructed reflectometer will be presented.
Effect of Impurities on the Interfacial Tension and Density of CO₂-Rich/Water Systems at HP/HT Conditions

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Interfacial properties in partially miscible phases play a major role in several chemical and reservoir engineering applications. Liquid–vapour and liquid–liquid interfacial tensions in CO₂-rich/water systems are, among others properties, of great importance when describing multiphase reservoir flows associated with enhanced oil recovery (EOR) and carbon capture and storage (CCS) as this property can greatly affect several rock properties. In general, CO₂ streams used in EOR and/or CCS operations come from capturing processes and can contain impurities such as methane, nitrogen, hydrogen and oxygen, among others. Despite its key role in water-alternating-gas (WAG) processes and direct influence on the CO₂ storing capacity of a potential reservoir, experimental data on the effect of impurities on the interfacial tension (IFT) of carbon dioxide / water systems are still limited. In this communication, our Pendant Drop facility was used to measure IFT values of water and three CO₂-rich multicomponent mixtures containing different species and content in impurities (up to 10% mol/mol). The phase densities, required to determine pertinent and accurate IFT values, were determined by measuring the oscillation period of the equilibrated phases with an Anton Paar densitometer at the experimental conditions of interest. The results showed a high pressure dependency of IFT values below the saturation point of CO₂ whereas a slight decrease on the interfacial tension was observed for higher pressures. The increase of content in light components resulted in generally higher gas-water IFT values comparing to that of pure CO₂ and in a reduction of the density of the CO₂-rich mixtures in particular at the CO₂ saturation conditions. Altogether, novel IFT and density measurements in CO₂-rich/water systems were performed for temperatures ranging from 25 to 150 °C and pressures up to 70 MPa.
Betaine as a foam booster has been shown to be able to increase the efficiency of surfactant foam enhanced oil recovery process. By mixing betaine with anionic surfactants, the stability of foam generated can be increased dramatically even in the presence of oil, which acts as a foam destruction agent. However, the mechanics behind the role of betaine as a foam booster is still unclear. Molecular dynamics simulations have been performed on air/water/surfactant interfaces and water/oil/surfactant interfaces to study the synergism between lauryl betaine (LB) and sodium alpha olefin sulfonate (AOS). To be specific, the microscopic structures of the surfactant monolayers formed with different LB to AOS ratio at an air/water interface and a water/oil interface have been investigated. Also, the umbrella sampling technique has been used to investigate the strength of interaction between surfactants in the surfactant monolayers with different LB to AOS ratio. The stability of film stabilized by surfactant monolayer with different LB to AOS ratio has been studied. It has been shown that highly structured monolayers can be formed from the mixture of LB and AOS, indicating synergism between surfactants. There exists an optimal LB to AOS ratio at which the strength of interaction between LB and AOS and the stability of films reach a maximum.
Development of a New Certified Reference Material for Thermal Diffusivity Measurements

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The flash method is one of the most popular methods to measure thermal diffusivity [1]. The National Metrology Institute of Japan (NMIJ) in AIST has been studying the laser flash method in order to establish the SI traceable thermal diffusivity standard [2,3]. We have developed key technologies to reduce uncertainty in laser flash measurements [2]. We have established the SI traceable thermal diffusivity measurement procedure and started to a calibration service with the quality management system along to ISO 17025. Using these techniques, a reference material consist of four isotropic graphite specimens for thermal diffusivity measurements (NMIJ CRM 5804-a) that was produced according to ISO Guide 34 was developed and supplied. The thermal diffusivity of the reference material shows from $1.3 \times 10^{-5}$ m$^2$s$^{-1}$ to $1.0 \times 10^{-4}$ m$^2$s$^{-1}$ in the temperature range from 300 K to 1500 K. There are many thermal diffusivity data from the order of $10^{-7}$ m$^2$s$^{-1}$ to the order of $10^{-3}$ m$^2$s$^{-1}$ are reported in the scientific journals and data books [4]. In order to cover the wide range of thermal diffusivity measured by the flash method, various reference materials are required. There is a need of a new reference material which shows lower thermal diffusivity rather than the CRM 5804-a. We have investigated some materials and selected a black ceramics as the candidate for a new certified reference material. The disk-sets of different thickness specimens of the ceramics based on Al2O3 and TiC were prepared. Some specimens were sampled and measured in order to determine thermal diffusivity. And homogeneity and stability was also investigated. The thermal diffusivity of the new reference material was determined as a function of temperature from 300 K to 1000 K. The homogeneity of it was evaluated as the standard deviation of thermal diffusivity at room temperature of some sampled specimens. The range of thermal diffusivity value is from $2 \times 10^{-6}$ m$^2$s$^{-1}$ to $1 \times 10^{-5}$ m$^2$s$^{-1}$ dependent on temperature and the expanded uncertainty are 5 % ~ 8 % with a coverage factor $k = 2$. The reference material should be used in vacuum or in inactive gas flow. The reference material is a set of three disk-shaped specimens with 10 mm in diameter and 1 mm, 2 mm and 3 mm in thickness. It will be start to supply in 2015. It is important to discuss on how to use these reference materials. We will discuss about the topics, for example validation of minimum heat diffusion time of the apparatus and estimation of uncertainty.

References

Thermal barrier coatings (TBCs) are used as heat and wear shields of gas turbine blades. There are strong needs to evaluate thermal conductivity of coating for thermal design and use. Thermal conductivity of the bulk material is obtained as the product of the thermal diffusivity, the specific heat capacity and the density above room temperature in many cases. The TBC consists of ceramics-based top-coat and bond-coat on the metal substrates in many cases. Usually, the thermal conductivity of thickness direction was focused because the heat mainly diffuses from the surface of the top-coat to the substrate. However, there are some hot spots on the gas-turbine wings related to temperature gradient in the turbine. According to this, we considered that the in-plane thermal conductivity also important for the thermal design of the gas turbine. The top-coat samples were prepared by plasma spray processing for this study. These were self-standing samples removed from substrates. We measured thermal diffusivities along to thickness direction and in-plane direction of these samples using the laser flash method and the periodic heating method. For in-plane thermal diffusivity measurement by the periodic heating method, the frequency and sample thickness were important factors in order to obtain reasonable results. It was found that thermal diffusivity of the top-coat was anisotropic. The microstructure of the sample was observed by the scanning electron microscope. There were many splats and micro cracks in the coating. We confirmed a relationship between anisotropy of thermal diffusivity and micro-structure of the ceramics-based top-coat of TBC.
Asphaltenes are the heaviest and most complex fraction of the crude oil. They are polydisperse and are defined as a solubility class which is soluble in aromatic solvents and insoluble in n-alkanes. Asphaltenes can precipitate and deposit in wellbores due to changes in temperature, pressure and composition. Such asphaltene deposition problems reduce the oil production and cost millions of dollars in mitigation and remediation efforts. Our group focuses on the development and implementation of advanced thermodynamic models and experiments to address the thermo-physical characterization and the phase behavior of crude oils in general and asphaltene precipitation in particular. Solubility parameter significantly influences the asphaltene precipitation behavior and is therefore a critical parameter in the context of understanding flow assurance issues related to Asphaltenes. This work focuses on the exploration of the solubility behavior of asphaltenes in various model crude oil samples at a molecular level by calculating solubility parameters of the mixtures over a wide range of temperatures and pressures. Based on previous work, the solubility parameter can be correlated with the density and the refractive index at ambient conditions. By measuring the density and the refractive index data, experiments can be executed to evaluate the solubility parameter at ambient conditions. Using this information and advanced equation-of-state modeling, solubility parameters over wide range of temperatures and pressures (covering reservoir/wellbore conditions) are calculated and will be presented. Molecular dynamics simulations in predicting solubility parameter values of solvent mixtures and asphaltene molecular models under reservoir conditions will also be presented.
Experimental measurements for methane hydrate phase equilibria containing salts, such as sodium chloride (NaCl), potassium chloride (KCl), ammonium chloride (NH₄Cl), and calcium chloride (CaCl₂), each separately, were performed up to about 10 wt%. The conventional isochoric method with continuous heating to measure hydrate phase equilibria in presence of salts was found to be unsuitable for making precise and accurate measurements due to the continuously changing salt concentration during hydrate formation and dissociation. As such, a modified isochoric method using a step-wise increase in temperature with sufficient equilibration time at every step was introduced to overcome these challenges for measuring the hydrate equilibrium conditions for systems containing salts. To confirm the accuracy of the modified isochoric method, high-pressure differential scanning calorimetry (DSC) was also used to measure the hydrate equilibrium conditions in the same salt systems using an equivalent step-wise method. The results from both modified isochoric and DSC methods showed good agreement with each other. The measurements performed considered salt concentration at the same ionic strength, so that the effectiveness of different salts could be compared. At the same ionic strength, the more effective salt for inhibiting hydrates are: NaCl > KCl ~ NH₄Cl. Based on these results, it can be suggested that hydration forces between the salt ions and water molecules disrupt the hydrogen bond network among water molecules and thus suppressing hydrate formation. Although all monovalent cations, such as sodium, potassium, and ammonium might be effective for hydrate inhibition, the strength of hydrate inhibition will depend on ionic radius of cations with same molality.
Spectral Stray Light Effect on High-Temperature Measurements Using a Multi-Color Pyrometer

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Non-contact optical measurements of high temperature objects are of great importance in applications. Optical pyrometry based on one-color or two-color measurements is well developed to determine surface or volume temperatures. As an improvement over one-color or two-color pyrometry, multi-color pyrometry has been used to determine temperatures which can greatly reduce the effect of the uncertainty in the spectral emissivity. It’s well known that the spectral stray light is a major, non-negligible error source affecting spectral intensity measurements for optical instruments. The purpose of this study is to investigate the effects of spectral stray light on high-temperature measurements using a multi-color pyrometer. The spectral stray light corrections were measured using a pulsed tunable laser for wavelengths from 0.41 μm to 2.63 μm. The spectral response characteristics of the pyrometer were calibrated using a standard high-temperature blackbody source. The experimental results show that the spectral response characteristics are approximately identical for different calibration temperatures when the spectral stray light correction is used. The corrections for the spectral stray light significantly improve the accuracy of the multi-color pyrometer at a blackbody calibration temperature which gives a simplified accurate calibration procedure, unlike the temperature calibrations for general optical pyrometers. Temperature measurement tests using a multi-color pyrometer for standard high-temperature source further verified the measurement accuracy of the calibrated pyrometer which also illustrates the necessity of the spectral stray light corrections for the complex optical pyrometer and the applicability of the multi-color algorithm.
Simultaneous Measurements of Total Hemispherical Emissivity and Thermal Conductivity of Metals at High Temperatures

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The total hemispherical emissivity is an important thermophysical parameter for thermal analyses and many types of measurements in research and engineering applications. This paper presented a method to simultaneously measure the total hemispherical emissivity and the thermal conductivity of metals at high temperatures using a steady-state calorimetric technique. The inverse problem to determine the emissivity and thermal conductivity from steady state high-temperature calorimetric experiments was established based on models for these two quantities assuming to be linear functions of temperature over a limited temperature range. The accuracy of the inverse solution was numerically analyzed for various noise levels for samples with various thermophysical properties. The noise in the total heat flux magnifies the result uncertainty so the solution accuracy was affected by not only the solution method itself, but also the noise in the “measured” data. The simulation results also illustrate that the calculation accuracies for the emissivity and thermal conductivity strongly depend on the proportions of the radiation and conduction heat fluxes in the strip sample arising due to the temperature distributions in the sample. Steady state high-temperature experiments with nickel samples were used to experimentally verify the method. The inverse solution results for the emissivity and thermal conductivity calculated from the measured data agree well with reported data in the literature. This research provides a useful reference for measuring the total hemispherical emissivity and thermal conductivity of conductive samples at high temperatures.
Thermal Conductivity of Metallization Via’s used in Microelectronic Packages

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In conventional co-fired multilayer alumina microelectronic packaging, the thick film refractory metallization via’s used for electrical signal routing also play a role in thermal conduction. This is seen with the common use of a thermal via array. What is less known is the quantitative thermal dissipation improvement due to the metallization structures. Answering this question poses experimental challenges as the co-fired metallization properties cannot be measured independently due to the sintering process interaction with the ceramic body. A quick inspection of the metallization electrical resistivity when compared to elemental tungsten provides insight into this change of physical properties. In the present study, a test coupon containing a high volume fraction of .1 mm diameter via’s was measured using the laser flash method. The rear surface transient temperature response curve was then correlated to a unit cell finite element model by varying the metallization thermal conductivity until the low frequency component of the residual error was minimized. Validation of the technique will be discussed using a geometrically (i.e. well controlled) simple periodic metallization/alumina laminate structure used to characterize the in-plane metallization thermal conductivity.
Homogeneous Nucleation of Carbon Dioxide by Molecular Simulation

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Homogeneous nucleation of carbon dioxide is considered by molecular simulation of large systems, regarding both the pure fluid as well as mixtures with carrier fluids, such as air, which do not participate in the phase transition significantly. Canonical ensemble molecular dynamics simulation using the Yasuoka-Matsumoto method [1] is applied to nucleation in supersaturated vapors that contain more carbon dioxide than at saturation [2]. Furthermore, bubble formation in metastable liquids is simulated. Beside the nucleation process, the agreement of model predictions with experimental data is evaluated for vapor-liquid equilibrium properties, including the surface tension, of pure carbon dioxide as well as mixtures with practically relevant carrier fluids. Multi-criteria optimization is employed to assess the capacity of 2CLJQ models, which contain two Lennard-Jones sites and a point quadrupole, to reproduce both bulk and interfacial properties accurately. The set of all Pareto-optimal parameter combinations is computed, so that suitable molecular models can be tailored to the requirements of a particular application [3]. Simulation results for the carrier fluid influence on the nucleation rate are compared with the extension of the classical nucleation theory (CNT) by Wedekind et al. [4], which accounts for a pressure effect. It is confirmed that the presence of air as a carrier decreases the nucleation rate. However, this influence is significantly weaker than predicted by CNT. Furthermore, CNT predicts a temperature dependence of the nucleation rate in the spinodal limit, which is not found in the present molecular dynamics simulations.

References

Stability of Mixed CO₂/CH₄ Hydrates

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The presence of vast deposits of methane hydrates on the seafloor has for some time been considered a viable source of non-renewable energy. Additionally, the methane guest molecules occupy the same hydrate structure, sl, as would carbon dioxide. It has therefore been suggested that one can harvest CH₄, while at the same time depositing CO₂, leaving the hydrate structure intact. This could then fulfill a dual purpose of energy gathering and climate gas storage. However, for such an undertaking to be reasonable, one should make sure that the resulting hydrate remains thermodynamically stable at the reservoir conditions. To obtain an understanding of how the stability is affected by alterations to composition, we have calculated the Gibbs energy difference at reservoir conditions between a filled hydrate and a liquid water/guest molecule mixture, using Monte Carlo simulations. The Gibbs energy landscape as composition changes is then used to evaluate how stability is affected when CH₄ is replaced by CO₂ in the cages. Finally, we calculate the energy barriers associated with moving through cages, and use these to evaluate the speed at which an exchange, or a potential decomposition, might occur.
Thermal Decomposition of Lower-GWP Refrigerants

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The use of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) has been widely restricted. They have been replaced with hydrofluorocarbons (HFCs) in order to protect the ozone layer. However, the leakage of refrigerant into air from active or end-of-life air conditioners has been a serious environmental issue owing to the high global warming potential (GWP) of HFCs. It has therefore been widely recognized that the replacement of HFCs with lower-GWP refrigerants is a reasonable solution of the problem. In Japan, the lower-GWP refrigerants such as R1234yf and R32 are considered as candidate alternatives for conventional HFC refrigerants. However, these lower-GWP refrigerants are often chemically unstable. To assess the risks when lower-GWP refrigerants are exposed to high-temperature solid surface, it is necessary to clarify their decomposabilities and products. However, the high reactivities of products like hydrogen fluoride (HF) make this quantification difficult. Moreover, in case of combustion, some researchers proposed that the reactivity of a molecule with more fluorine atoms than hydrogen atoms, like R1234yf, is affected by humidity. Thus, its flammability limits and product composition are influenced by temperature and humidity. In this study, to discuss on the effects of temperature and humidity in thermal decomposition, mixtures of refrigerants and air were decomposed in heated tube and the products were analyzed with FT-IR to quantify decomposed refrigerants and hydrogen fluoride which was the main toxic product. The tested refrigerants were R1234yf, R32, R134a and R22. The temperature of the heated tube and humidity in the mixture were systematically changed. Because the concentration of hydrogen fluoride was influenced by the tube material due to the chemical reaction between hydrogen fluoride and the tube material, several kinds of heated tubes, made with stainless steels and Inconel alloy, were used. The thermal decomposition characteristics of lower-GWP refrigerants were compared with those of conventional non-flammable refrigerants.
Phototacoustic and Photothermal Phenomena in Complex Porous Media

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Nowadays, porous materials are indispensable for their practical application in sensorics devices and specified chemical reactors. Moreover, the porous semiconductors are perspective as active elements of optoelectronics devices and efficient photoelectrical convertors. It is clear that thermal, transport and mechanical properties of porous media play a crucial role for ensuring reliability of such devices. Porous materials characterize by an important specific surface and complex fractal-like morphology, thus such materials study require some features. Photothermal and photoacoustic techniques are especially useful methods for porous media investigation, because the excitation of informative response in this case is noncontact. In this paper, we overview peculiarities of such methods application for porous materials study. As model samples the widely used porous silicon based structures were chosen. The photoacoustic signal formation in such inhomogeneous media in the cases of most convenient gas-microphone and piezoelectric methods was analyzed as in frequency- as in time-domain. The main emphasizes on the resolving of inverse problems for evaluation of thermal and mechanical parameters were made.
Numerical process simulations, such as power-plant design with heat-cycle calculation software, flow analysis with computational fluid dynamics (CFD), and real-time process optimizations, are widely used in power engineering. These simulations are computationally intensive, especially when transient processes are considered. The calculation of thermodynamic properties from fundamental equations is very time-consuming and leads to unacceptable computing times in complex process simulations. Therefore, property calculations are often simplified through the use of the ideal-gas equation or a cubic equation of state. Depending on the range of state, these simplifications cause inaccuracies in the results of the process simulation. In order to provide property calculation algorithms for computationally intensive simulations, the Spline-Based Table Look-up Method (SBTL) was developed in a project of the International Association for the Properties of Water and Steam (IAPWS). The SBTL method applies polynomial spline interpolation techniques and specialized coordinate transformations to reproduce the results of an underlying formulation, e.g., the industrial formulation for water and steam IAPWS-IF97, with high accuracy and low computing time. Furthermore, so called inverse spline functions enable the calculation of backward functions from their corresponding forward spline functions with complete numerical consistency. The new “IAPWS Guideline on the Fast Calculation of Steam and Water Properties with the Spline-Based Table Look-Up Method (SBTL)” contains detailed information on the SBTL method. Furthermore, it contains SBTL property functions for calculations from specific volume and specific internal energy (v,u), as required in CFD. By means of inverse spline functions, numerically consistent property functions of (p,v) and (u,s) are calculated. Moreover, SBTL property functions of pressure and specific enthalpy (p,h), as used in heat-cycle simulations, and the corresponding backward functions of (p,T), (p,s), and (h,s) are provided. The maximum deviations of the SBTL functions from the underlying IAPWS formulations are less than 10-100ppm. With regard to IAPWS-IF97, computations from the (v,u) spline functions are more than 150 times faster. The applicability of the SBTL method has been tested in the CFD software TRACE, developed at DLR, and in heat-cycle calculations. The results of these tests show negligible differences to those obtained from simulations with IAPWS-IF97, but the overall computing times are reduced significantly.
A comprehensive thermodynamic model has been developed for calculating the thermodynamic properties of aqueous mixtures containing amines and amine hydrochlorides. Various amines, including alkylamines, alkanolamines, and heterocyclic nitrogen derivatives are commonly used to neutralize acidic streams in refinery column overhead units. However, the presence of amines in combination with hydrogen chloride may lead to the formation of solid or concentrated aqueous amine hydrochloride phases, which may cause corrosion problems.

Thermodynamic modeling offers the possibility of rationalizing and preventing the formation of amine hydrochlorides in multicomponent mixtures containing amines, water, hydrocarbons, hydrogen chloride, and other acid gases. For this purpose, the previously developed Mixed-Solvent Electrolyte (MSE) model has been extended to amine and amine hydrochloride systems, which may show vapor-liquid, solid-liquid and solid-gas equilibria in aqueous environments. The MSE model represents both solution speciation and phase equilibria. Standard-state properties of individual species are calculated from the Helgeson-Kirkham-Flowers equation of state whereas the excess Gibbs energy includes a long-range electrostatic interaction term expressed by a Pitzer-Debye-Hückel equation, a virial coefficient-type term for interactions between ions and a short-range term for interactions involving neutral molecules. The combined model accurately represents experimental phase equilibrium and pH data for systems ranging from dilute aqueous solutions to pure solid or fused liquid amine hydrochloride phases.

When applied to multicomponent systems encountered in refinery overheads, the model can be used to simulate the changing phase behavior of condensing streams, which may include stability regions of a gas phase, a concentrated amine hydrochloride ionic phase, a dilute aqueous phase, a volatile solid phase, and a hydrocarbon-rich liquid phase.
NIST calibrates gas flow meters with ranges up to 2000 L/min by generating a steady flow through the meter under test and then diverting the downstream flow into a carefully thermostatted, 0.677 m³ collection tank for a measured time. The quantity of gas collected is measured with an uncertainty of 0.013 % using the gas’s equation of state, measurements of the temperature and pressure, and the volume of the thermostatted tank. For larger range flow meters it would be simpler and faster to calibrate them by using a larger thermostatted, collection tank (for example, 10 m³). However thermostatting such a tank is expensive. The present work shows that we can accurately determine the volume of gas within a large, off-the-shelf, commercially manufactured, un-thermostatted tank. Using microwave techniques that are scalable to very large volumes, we measured the interior volume of a 0.3 m³, commercially manufactured pressure vessel with a relative uncertainty of 0.06 %, as confirmed by independent, more-accurate gas-expansion measurements. This pressure vessel (or a much larger one of a similar design) could be used as either a calibrated volume standard or as a gas source and/or a gas collector for the calibration of gas-flow meters. In addition, we determined the expansion of the vessel with temperature \( (\partial V/\partial T)_p/V = \frac{(35.3 \pm 1.9) \times 10^{-6}}{\text{K}^{-1}} \) and we estimated the pressure expansion \( (\partial V/\partial p)_T/V = 0.9 \times 10^{-3} \text{ MPa}^{-1} \). The volume measurement did not require careful thermostatting; its uncertainty was dominated by imperfect modeling of the volume’s shape.
Obtaining the Thermal Diffusivity of Human Dentin and Enamel

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Using the model of thermal diffusion of Rosencwaig and Gersho which consists in making influence modulated radiation from a source, on the sample, the absorbed radiation generates inside thermal waves, which, to be detected are transformed into an electrical signal which is amplified and stored for further analysis, determines the thermal diffusivity of human dentin and enamel using the photo acoustic technique diffusion of heat settings. The results obtained indicate that the crystallinity in enamel and dentin porosity are important factors that influence the diffusion of heat through both since this is a process by which a type molecules across a plane and mingle with other molecules, as it is the case of enamel and dentin being higher when the flow takes place in the direction of porosity.
We compare methods for determining the dew-point density and pressure of fluid mixtures. In this context the \((p, \rho, T, x)\) behavior of three (methane + propane) mixtures was measured with a two-sinker magnetic suspension densimeter over the temperature range of \((248.15\) to \(298.15)\) K; the data extended from low pressures into the two-phase region. The compositions of the gravimetrically prepared mixtures were \((0.74977, 0.50688, \text{ and } 0.26579)\) mole fraction methane. We analyzed isothermal data in three ways: (1) in a “traditional” analysis the dew point was given by the intersection of a virial fit of the \((p \text{ vs. } \rho)\) data in the single-phase region with a linear fit of the data in the two-phase region; (2) an analysis of the adsorbed mass on the sinkers versus pressure yielded a sharp discontinuity at the dew point; and (3) an analysis of the “coupling constant” \(\varphi\) (related to the force transmission error of the magnetic suspension coupling) also yielded a sharp discontinuity because of condensation onto the sinker. The “traditional” analysis suffered from an indistinct change in the slope, resulting in relatively high uncertainties. The “adsorbed mass” analysis provided a good determination of the dew-point pressure, but at the expense of an increased uncertainty in the dew-point density, because the data from one of the sinkers was required to determine the adsorbed mass. The “coupling constant” analysis yielded an accurate pressure while retaining the full density accuracy of the two-sinker technique. By comparison, a traditional isochoric experiment resulted in larger uncertainties in the dew point, due in large part, to the continuously changing temperature. We conclude that the analysis of the data determined for the coupling constant throughout an isothermal experiment provides an accurate determination of the dew point temperature, pressure, and density. However, a two-sinker instrument is required.
We describe a new instrument for the measurement of liquid-phase speed of sound. It is based on the dual-path, pulse-echo technique and operates over a temperature range of –45 °C to 150 °C, with pressures to 90 MPa. A quartz crystal with a resonant frequency of 8 MHz sits in a sample volume 24 mm in diameter by 42 mm long; the path lengths are 12 mm and 30 mm. Several novel design features permit the entire transducer assembly (crystal, sample volume, and reflectors) to fit in a pressure vessel with internal dimensions of 29 mm diameter by 165 mm deep; the total volume of sample required is approximately 25 mL. The (transducer + pressure vessel) assembly is placed in a liquid bath for temperature control. The input pulse is a modulated sine wave consisting of 10 to 20 cycles and is generated by an arbitrary function generator. The speed of sound is calculated from the time difference between the short-path and long-path echo signals, as recorded by a digital storage oscilloscope. We make use of the signal-processing capabilities of the oscilloscope to automatically record only the actual echo signals, discarding the “dead time” between the echoes. The echo data, together with temperature and pressure data, are stored for off-line analysis of the speed of sound. The path lengths were calibrated with measurements on water, and measurements on propane serve to verify the performance of the instrument.
A model of nanocrystal in the form of a rectangular parallelepiped with a variable surface shape (RP-model) is used to study of the dependencies of the modulus of elasticity, Poisson’s ratio, Young’s modulus, shear modulus, coefficient of thermal expansion and heat capacity versus of size and shape of the free-standing nanocrystal of the simple matter. The concrete calculations are done for diamond, silicon and germanium. It is shown that at the isomorphous decrease of size for nanocrystals of diamond, Si or Ge the values: modulus of elasticity, Young’s modulus, and shear modulus are decreasing, but functions: Poisson’s ratio, coefficient of thermal expansion, and heat capacity are increasing along isotherm. Than nanocrystal shape deviates from the most energetically stable shape (for RP-model it is cube), the more noticeably the changes of mentioned functions at the decrease of the nanocrystal size along of isotherm. The calculations for the nanocrystal of silicon have shown that at the isomorphous reduction of size along isotherm of 100 K the coefficient of thermal expansion at defined size passes from the negative into the positive field.
The Changes of Thermophysical Properties of Iron under Isothermal Compression

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Coming from the pair potential of interatomic interaction in the Mie–Lennard-Jones form, and the Einstein’s model of crystal, without of the fitting parameters the state equation and the baric dependencies of thermophysical properties are received for BCC iron. The calculations were executed along two isotherms: 300 and 1500 K, for pressure from zero till 8000 kbar, i.e. for the relative volume from 1 up to 0.5. The good coincidences with experimental data are received. The graphs of baric dependencies for the next thermophysical properties are calculated: for the Debye temperature, for the first, second and third Gruneisen parameters, for the isothermal compression modulus and for its derivative with respect to pressure, for the isochoric heat capacity and for its derivative with respect to pressure, for the coefficient of thermal expansion and for its derivative with respect to pressure, for the isobaric heat capacity, for the specific (per unit area) surface energy and for its derivative with respect to pressure. It was shown that for ultrastrong compression the next regularities are carried out: the dependencies from pressure for the Debye temperature and for the second Gruneisen parameter tend to maximum, the dependencies from pressure for the first and for the third Gruneisen parameters go to zero, the dependencies from pressure for the isothermal compression modulus and for the specific surface energy are changing by a linear manner, the dependency of the coefficient of thermal expansion from pressure tend to constant value.
The Changes of Thermophysical Properties of Iron under Isothermal Compression

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Coming from the pair potential of interatomic interaction in the Mie–Lennard-Jones form, and the Einstein’s model of crystal, without of the fitting parameters the state equation and the baric dependencies of thermophysical properties are received for BCC iron. The calculations were executed along two isotherms: 300 and 1500 K, for pressure from zero till 8000 kbar, i.e. for the relative volume from 1 up to 0.5. The good coincidences with experimental data are received. The graphs of baric dependencies for the next thermophysical properties are calculated: for the Debye temperature, for the first, second and third Gruneisen parameters, for the isothermal compression modulus and for its derivative with respect to pressure, for the isochoric heat capacity and for its derivative with respect to pressure, for the coefficient of thermal expansion and for its derivative with respect to pressure, for the isobaric heat capacity, for the specific (per unit area) surface energy and for its derivative with respect to pressure. It was shown that for ultrastrong compression the next regularities are carried out: the dependencies from pressure for the Debye temperature and for the second Gruneisen parameter tend to maximum, the dependencies from pressure for the first and for the third Gruneisen parameters go to zero, the dependencies from pressure for the isothermal compression modulus and for the specific surface energy are changing by a linear manner, the dependency of the coefficient of thermal expansion from pressure tend to constant value.
During the last years carbon nanotubes (CNT) have attracted great interest due to their outstanding electrical, magnetic, mechanical, thermal, and optical properties. CNT represent one of the most recently found allotropic forms of carbon having a high degree of constitutional organization. On the other hand, decorating CNT with magnetic particles has also attracted great attention due the possibility of manipulating the CNT using an external magnetic field. This characteristic makes them especially interesting due to its potential in changing the thermal properties of fluids in which decorated CNT are immerse. In this work the response of magnetic solutions, made of ethylene glycol as solvent and magnetite decorated CNT (m-CNT) as solute in different concentrations, were studied using the photoacoustic (PA) technique. The samples were mounted on a metallic surface in a modified Rosencwaig photoacoustic cell and the PA signal was registered as a function of time and at a fixed modulation frequency when the sample is subjected to an external magnetic field of 150 Gauss. The experiments show an increment in the PA signal, for the case of the magnetic field parallel to the laser beam and a decrease in PA signal for the case of the magnetic field perpendicular to the laser beam. It is shown that the observed phenomena can be understood using a two-layers model considering that the carbon nanotubes can be aligned along the external magnetic field forming a column-like structure.
A Novel Method to Investigate the Dew Line and Sorption Effects of Binary Mixtures Using a Modified
Two-Sinker Densimeter

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We present a new technique for accurately determining the dew line of binary mixtures and for investigating sorption effects when approaching the dew line. To realize the new technique, we modified the NIST two-sinker densimeter by incorporating a new pair of sinkers. In contrast to the original sinkers, the new ones were of the same material (titanium), same mass, and same volume, but they had different surface characteristics, which allowed for a quantitative determination of the mass of sample adsorbed onto the sinker. Measurements of the \((p, \rho, T, x)\) behavior were carried out on binary mixtures of (methane + propane) and (argon + carbon dioxide) in the temperature range from \((248.15 \text{ to } 298.15)\) K starting at low pressures and extending into the two-phase region. With the new sinkers, sorption effects on the order of 10 μg could be measured; hence, the idea of using special sinkers has been proven successful. As the pressure was increased towards the dew point along an isotherm, three distinct regions were observed: Far away from the dew point, the adsorbed mass was on the order of a few ten’s of μg; within approximately 98 % of the dew point pressure, the adsorbed mass increased sharply (up to a few hundred μg); finally, a further, sharper increase in adsorbed mass (up to a few mg) occurred. We speculate that the second region corresponds to capillary condensation (also called pre-condensation), and that the transition from the second to the third region corresponds to bulk condensation onto the sinkers, thus being the true dew point. Further work will be required, however, to confirm this hypothesis and to model it.
The Physikalisch-Technische Bundesanstalt (PTB) provides emissivity measurements over a wide range of temperature. Until recently the temperature ranges covered were by a setup under vacuum from -40 °C to 450 °C and by a dynamic emissivity measurement from 800 °C to 2000 °C. To bridge the gap we designed and optimized a sample holder operating between 50 °C and 1000 °C. A prerequisite for low uncertainties in emissivity measurements is a homogeneous temperature distribution on the sample surface. So, the main task of the development of the new high temperature sample holder was to find the optimum sample holder geometry and heating concept to reach the planned temperature up to 1000 °C with optimized temperature homogeneity. The sample itself and therefore its surface emissivity affect the temperature homogeneity. The challenge was to evolve a heating concept which is able to vary and optimize the surface temperature homogeneity for various surface emissivities. The thermal conductivity and emissivity of the sample holder, given by the material, its geometry and the heating concept were varied to find a solution. Simulations were done for three different materials: INCONEL® alloy 600, Nickel 200 and pure Molybdenum with different geometries and multiple heating zones. The identified concept features two heating zones: one at the back side and one at the curved shell of a cylindrical body. The sample holder is made from Molybdenum which allows reaching the desired temperature of 1000 °C at the sample surface due to its high thermal conductivity and its low emissivity compared to INCONEL® 600 and Nickel 200. Additionally we have designed an optimized two stage radiation shield to reduce radiation losses of the holder to lower the necessary heating power for reaching a maximum temperature of 1000 °C. First results of emissivity measurements will be shown at the conference.
Evaluation of New Chemical Compounds as Low Dosage Hydrate Inhibitors

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Plugs caused by gas hydrate formation are a great problem in the oil and gas industry. Low dosage hydrate inhibitors (LDHIs) are part of a developed hydrate control technology. Two classes of LDHIs are known, kinetic inhibitors (KHIs) and antiagglomerants (AAs). Several different specific LDHIs are already being successfully used in the field. This work presents results on the performance of some newly synthesized chemical compounds. In the present work the experiments to determine the performance of the new chemical compounds were carried out in a device that has a high-pressure stainless steel cell with sapphire windows and temperature and pressure probes logged on a computer to obtain results as function of time. The method used is the constant cooling test, with a rate of 2 °C/h. After the cooling, the warming was 5 °C/h. At least four cooling-warming cycles were carried out to verify the reproducibility of results and minimize the stochastic effect. The method is based on the drop of pressure as temperature decreases with which, it is possible to detect the pressure change due to the formation of the natural gas clathrate hydrate. Also, it is possible to determine by comparison with a reference system, in diagrams temperature vs time and pressure vs time, the efficiency of the new low dosage hydrate inhibitors at known concentrations, at the initial pressure of 6 MPa and in the temperature range of (293.15 to 274.85.15) K. The experimental results show a positive performance as LDHIs for some of the evaluated compounds in the concentration range (0.5 to 1.0) mass % and at relatively large subcooling temperature.
Numerical Investigation on the Fuel Spray Processing for the Mild Combustion

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Mild combustion is recently attracted attention of many researchers in the fields of combustion and internal combustion engines. The importance of the mild combustion is because of existing of low temperature flame in this kind of combustion and consequently less production of major pollutants like NO\textsubscript{X} and also increasing of the combustion efficiency. In this paper a numerical investigation is carried out for providing a fuel spray for the mild combustion. AVL FIRE software is used for the numerical simulation of the problem. The key idea in this research is providing a relatively strong vacuum region inside the fuel spray plume and consequently suction of more ambient air into the fuel spray which in turn provides a lean mixture of the fuel and air and decreases the temperature of the flame. Lean mixture of the fuel and air in conjunction with reduction of flame temperature provide proper conditions for the mild combustion of the fuel and consequently decrease the major pollutants like NO\textsubscript{X} and increase the combustion efficiency.
Viscosity and density are thermophysical properties which are crucial to characterize any kind of fluid such as aqueous amines. These blends are becoming more and more relevant for its CO\textsubscript{2} capture potential, so it would be useful to know viscosity and density accurately. In this sense, it is possible to find in literature densities and viscosities of these mixtures at atmospheric pressure, but the task becomes more difficult when we try to find values at high pressures which could be interesting to manage in order to characterize these fluids completely.

TERMOCAL research group has a long experience in this type of measurements and it has recently involved in the development of two techniques for viscosities at high pressures (up to 140 MPa): a falling body viscometer (stainless steel falling cylinder) and a vibrating wire viscometer (tungsten wire). Therefore, viscosity and density measurements at high pressures (up to 120 MPa) and temperatures between 293.15 and 353.15 K of mixtures MDEA-water (from 10 \% to 40 \% MDEA mass fraction) will be presented in this work. Density measurements have been performed with an Anton Paar DMA HPM densimeter and it has been used the falling body technique for viscosities at high pressures because of its sturdiness in terms of corrosion.

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The accurate estimation of water-hydrocarbon vapour-liquid and vapour-liquid-liquid equilibrium is an important activity related to safe and reliable design of industrial equipment. Currently heavy, highly aromatic oil fractions are of interest due to the use of bitumen and heavy oil as feedstock and proper estimates for water in hydrocarbon, hydrocarbon in water and hydrocarbon in air concentrations are key parameters for process design and evaluation of new processes such as high temperature thermal upgrading using supercritical water. In addition to heavy hydrocarbon feedstock processing the correct estimation of water solubility in gaseous hydrocarbons as well as in liquid hydrocarbons is of interest for the gas production and midstream industries due to the possibility of gas hydrate formation in pipelines and ice formation in cryogenic distillation towers and the associated safety and efficiency problems. In addition, novel separation processes based on the formation of hydrates and ice require accurate quantitative models that can be used to calculate the amount of solids formed together with accurate fluid phase models for the calculation of water concentrations in the gas and liquid phases at equilibrium.

In this paper we present a simple and accurate equation of state model used for the calculation of water solubility in gas or liquid hydrocarbons, solubility of hydrocarbons in water and its use for the calculation of vapour-liquid-solid equilibrium. The model can be used to represent aqueous systems at low and high temperatures, is simple to use, can be used for the computation of consistent phase envelopes and is extensible to other types of mixtures.
The history of ionic liquids (ILs) effectively started in 1914, when the physical properties of ethylammonium nitrate ([CH₃CH₂NH₃⁺][NO₃⁻], m.p. 13-14 °C) were first reported. ILs are generally defined as salts composed of discrete cations and anions with melting points below 100 °C, and many are liquid at ambient temperature. IL research has grown rapidly over the past decade due to the realization that these materials have many unique properties such as negligible vapor pressure and outstanding solvation potential. Ionic liquids have been further emphasized by the fact that their physical and chemical properties can be finely tuned by varying both the cation and anion. Our research has focused on accurately measuring vapor-liquid equilibria (VLE) and vapor-liquid-liquid equilibria (VLLE) and using thermodynamic models to understand the phase behavior of binary gas mixtures in ILs. This presentation will focus on the importance of characterizing the global phase behavior of gases in ionic liquids and how this can provide insight into new applications. Solubility measurements of several gases in ILs will be discussed and important experimental details regarding VLE measurements using a gravimetric microbalance and VLLE measurements using a mass-volume technique will be highlighted. VLE data have been successfully correlated with a modified Redlich-Kwong equation of state (EOS), and in certain cases (e.g. hydrofluorocarbons) the EOS predicts partial immiscibilities (LLE) with lower critical solution temperatures (LCSTs) in the fluorocarbon-rich side solutions. We have also found that gases such as CO₂ can exhibit different solubility behaviors in ILs (i.e. physical and chemical absorption) and that these behaviors can be analyzed with the EOS using a simple association model and excess thermodynamic functions. Knowledge of gas and IL phase behavior has led to several practical applications including separation of azeotropic gas mixtures, removal of CO₂ from flue gas and new fluid pairs for absorption cooling. These along with other interesting examples from the literature will be discussed.
Asphaltenes are well-known for their tendency to precipitate and deposit during production of reservoir crude oils. Asphaltene precipitation determination is a key step in studying the asphaltene deposition problems since precipitation is a necessary condition for the asphaltenes to deposit. The methods developed so far (direct methods) to measure the onset of asphaltene precipitation require a minimum particle size - usually from about 0.5 to 1 µm. This means that asphaltene onset detection by direct methods can only occur after precipitated asphaltenes aggregate to exceed the detection limit. In this work, a novel experimental technique called “Indirect Method” is used for studying asphaltene precipitation on both model oil and real crude oil systems. This method, which is a combination of gravimetric and spectroscopy techniques, is proposed for determination of the asphaltene precipitation onset as well as the amount precipitated. The results obtained in this study show that the indirect method has three main advantages over direct methods. First, it can be applied for determination of both the onset and the amount of asphaltene precipitation. By having a proper calibration curve, the absorbance of the supernatant fluid after centrifugation step, can be easily and accurately related to the amount of precipitated asphaltene. Also, the indirect method can be used for crude oils ranging from very low to high asphaltene content; model oils studied in this work contained 0.1 wt% asphaltenes (considered as a low concentration) to 5 wt% asphaltenes (considered as a high concentration). Finally, the minimum particle size detected with the indirect method is smaller than with the direct methods, making the indirect method more sensitive to the size of precipitated asphaltene particles.
Present steel processing, interfacial phenomena between molten steel and oxides in which are usually called slag or mold flux, play important roles in materials design. For examples, in continuous casting, Marangoni convection due to the gradient of the interfacial tension between molten iron and molten oxide enhances heat transfer, and also avoid drop-off of oxide particles from flux into molten iron. Therefore, interfacial tension must be known for process controlling. From this requirement, we proposed the interfacial tension measurement technique between molten steel and oxides using the modified oscillating drop method with levitation techniques. The interfacial tension data using traditional technique based on the sessile drop method have been obtained only in temperature at melting temperature of iron due to dissolution of containers and the substrate into molten steel and oxides in higher temperature regions. Our propose technique to obtain temperature dependence of interfacial tension between molten iron and oxides is used a core-shell form droplet including interface between two liquids [1] using the electrostatic levitation, which can achieve the containerless conditions. However, since the difference of viscosity of molten steel and oxides are larger, the large viscosity difference affects on the surface oscillation of droplet [2]. Therefore, we performed numerical simulation of droplet oscillation of core-shell drops of molten iron and oxides, and we discussed the best conditions of droplet conditions including the viscosity value range for interfacial tension measurements from the outer surface oscillation frequency. The measurements will start late 2015 in International Space Station (ISS) using the electrostatic levitation furnace (ELF) in KIBO.

References

Measurements of Density and Structure of Alloys Liquids by Levitation Technique

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We have measured accurately the densities of high-temperature alloy’s liquids by electromagnetic levitation (EML) technique within the static magnetic fields. In the technique, the Lorentz force by the interaction between the liquid metals and the static magnetic fields reduces the surface oscillation and translational motion of samples. By the effect, we can precisely obtain the correct volume of levitated liquid samples like a solid body with reducing an order of magnitude compared with previously reported data using levitation technique. Using the technique, we obtained the density of high-temperature liquid of various alloys in the temperature range from 700 to 2400 K. We also performed the structural analysis of these liquids using high-energy x-ray diffraction by the synchrotron source of SPring-8 in Japan combined with the levitation technique. Diffraction data were analyzed by the reverse Mont Carlo (RMC) technique and the Voronoi polynomial analysis. From the accurate density data and structural analysis results, we discuss the density change with temperature and compositions from the viewpoints of liquid structure with atomic interactions in the liquid phases.
A Crossover Model Based on the Virial Equation of State

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The virial equation of state (VEOS) is a power series in density, with coefficients that can be determined from molecular considerations. Its rigorous connection to statistical mechanics makes it an appealing choice for many purposes, but its utility is limited to conditions where the series converges. Singular behavior in the equation of state, such as encountered upon approach to the critical point, restricts its range of application. In previous work, we took steps to address this problem by forming an approximant that explicitly incorporates this singular behavior while remaining fully consistent with the VEOS at low density. This treatment was shown to provide several new capabilities, including improved predictions of critical properties from the virial coefficients, refinement of critical properties given by simulation/experimental measurements, and an estimate of a critical amplitude for several fluids. Our previous work was restricted to the critical isotherm. In the present work, we enhance the approximant by including temperature dependence, allowing us to incorporate scaling along the critical isochore. The approximant is designed to enforce the correct singular behavior at the vapor-liquid critical point, while still retaining the correct temperature-dependent low-density behavior as expressed by the VEOS. The efficacy of the proposed equation of state is demonstrated for the square-well fluid, chosen for this initial study because the temperature dependence of its virial coefficients can be expressed analytically.
Accurate Measurements of the Superior Calorific Value of Methane by the Renewed GERG Calorimeter

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Due to the commercial transfer of billions of cubic meters of natural gases the knowledge of the superior calorific value of the main natural gases components is of outstanding interest. However, up to now the values given in ISO 6976 has been based on measurements made by Rossini[1] in 1931 and Pittam&Pilcher[2] in 1972. To establish more reliable values for the superior calorific values of methane and also of other main components of natural gases a Rossini-type reference calorimeter has been developed by Physikalisch-Technische Bundesanstalt (PTB) in Germany on behalf of the GERG-Association (Groupe Européen de Recherches Gazières). After the first measurements of methane, which confirmed the value given in ISO 6976 within the calculated uncertainty of 0.05 %, the GERG calorimeter was dismantled at PTB and moved to the thermodynamics institute at Ruhr-Universität Bochum. The necessary new setup of the GERG calorimeter has given us the chance for a very careful examination of both the hardware and the software of the GERG calorimeter. Some important improvements could be accomplished in both areas, which enabled us to significantly improve the precision of the obtained data. The resulting superior calorific value of methane agrees with previous measurements and assessments within the combined uncertainty, but is still significantly higher compared to experimental values reported most recently[3] and compared to the value given in ISO 6976, respectively. Based on a new approach that allows determining the mass of the burned gas by two methods (by online weighing of the flue gas and by weighing of the water absorbed during combustion and flushing), a systematic error in the Rossini-method can be demonstrated. This may have an impact on the superior calorific values of many hydrocarbons, as the Rossini-method has been widely used for their determination in the past century.

References

Effect of Agitation on Crystallization and Rheological Behavior of Super-cooled Calcium Silicate Based Melts Characterized by Electrical Capacitance Measurement

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The effect of agitation on the crystallization behavior of super-cooled calcium silicate melts were systematically investigated by the measurement of their electrical capacitance over a wide temperature range from liquid region to well below the liquidus temperature. It is well known that the electrical capacitance of liquids is generally much higher than that of solids owing to the differences in their respective polarization mechanisms. These differences were exploited as a sensitive indicator of the crystallization of molten calcium silicates in an experimental furnace equipped with an electrical capacitance measuring system. The system comprised a Pt-based alloy crucible and a rotating rod that allowed evaluation of the effect of agitation generated by the rod, connected to a capacitance meter. As expected, at a particular temperature, the electrical capacitance of the molten calcium silicates underwent a precipitous decrease by roughly three orders of magnitude, which was dependent on the chemical composition. This indicated the presence of crystallization and this was confirmed by corresponding microstructural characterization. It was also found that, for the measurements acquired with rotating rod agitation, the temperatures at which the capacitance underwent the sharp decrease were higher than that identified without the agitation. This suggests that the agitation effect induced by the rotating rod accelerates the crystallization of molten calcium silicates. Additionally, variation in the apparent viscosity of the super-cooled calcium silicate melts with dispersed crystalline phases will be discussed at the symposium.
Mesoscopic inhomogeneities in binary mixtures of ethyl-ammonium nitrate (EAN), a protic ionic liquid, and pentanol are investigated using Small Angle X-ray Scattering as a function of concentration and temperature ranging from 193 to 313 K. Both compounds are amphiphilic and characterized by an extended hydrogen bonding network; however, though macroscopically homogeneous, their mixtures are heterogeneous at the mesoscopic spatial scales. Two different species of mesoscopic inhomogeneities are observed: Critical concentration fluctuations, as observed in EAN/Octanol mixtures [1], and inhomogeneities caused by separation into ionic and non-ionic regions. The latter ones have been predicted by simulation [2] and verified experimentally [3] in ionic liquids containing cations with long hydrocarbon chains. In pure EAN such structuring into ionic and non-ionic regions gives rise to a band centred near $Q = 6.2 \text{ nm}^{-1}$ [4]. A similar band at $Q = 5.2 \text{ nm}^{-1}$ is also observed in pentanol, suggesting a segregation into polar and no-polar regions. In mixtures the inhomogeneity bands of EAN and pentanol match. When approaching the critical composition near the mole fraction $x = 0.5$ and lowering the temperature towards the critical temperature, the inhomogeneity band merges with a band centred at $Q=0$ that increases, when approaching the critical region. The concentration and temperature dependence of the $Q=0$ band have the characteristic features for critical fluctuations near the liquid-liquid upper critical solution point, and is thus attributed to critical concentration fluctuations. The critical temperature is estimated by extrapolation to $Tc\approx 190 \text{ K}$, which is located inside the solid phase and thus cannot be reached in the experiment.

References


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Zeolites play numerous important roles in modern petroleum refineries and have the potential to advance the production of fuels and chemical feedstocks from renewable resources. The performance of a zeolite as separation medium and catalyst depends on its framework structure and the type or location of active sites. To date, 213 framework types have been synthesized and >330000 thermodynamically accessible zeolite structures have been predicted. Hence, identification of optimal zeolites for a given application from the large pool of candidate structures is attractive for accelerating the pace of materials discovery. Here we identify, through a large-scale, multi-step computational screening process, promising zeolite structures for two energy-related applications: (i) with the ability to purify ethanol beyond the ethanol/water azeotropic concentration in a single separation step from fermentation broths and (ii) with up to two orders of magnitude better adsorption capability than current technology for linear and slightly branched alkanes with 18-30 carbon atoms encountered in petroleum refining. These results demonstrate that predictive modeling and data-driven science can now be applied to solve some of the most challenging separation problems involving highly non-ideal mixtures and highly articulated compounds.
Many methods in non-destructive evaluation image the samples interior structure from measured signals on the surface of a sample, like in photoacoustic imaging from measured pressure signals or in thermographic depth profiling from measured temperature signals. This imaging is an ill-posed or ill-conditioned problem, meaning that small errors in the measured surface signals can result in much larger errors in the reconstructed images. Typically the image reconstruction includes additional assumptions, such as the smoothness of the solution. This process is known as regularization, like truncated singular value decomposition (SVD) or Tikhonov regularization. The choice of an adequate regularization parameter which describes the trade-off between the original ill-conditioned problem and the additional assumptions (e.g. smoothness) is critical and has to be evaluated for every individual problem. For interior structures the information about the spatial pattern has to be transferred to the sample surface, where the signals are detected and the structures are reconstructed from the measured signals. The propagation to the sample surface reduces the available information for imaging, e.g. by scattering, attenuation, and diffusion. From statistical thermodynamics it is known that this information loss is for a macroscopic sample in a good approximation equal to the entropy production for the propagating wave from the samples interior to the surface. The entropy production is the dissipated energy divided by the temperature. We propose that by using the entropy production we get a physical background for choosing the regularization parameter for our imaging problem and no additional assumptions for regularization like smoothness or a minimal total variation of the reconstructions are necessary. These theoretical results are applied to compare photothermal and photoacoustic depth profiling. For thin coatings thermal and acoustic equations have to be coupled to model the measured surface dislocations and to get the adequate inverse problem for depth profiling.
Modern apparatuses for high pressure speed-of-sound measurements in fluids are based on transient techniques and, consequently on the determination of the time-of-flights of signals that traveled different distances. Considering that, due to the finite dimensions of the ultrasonic source, signals are delayed with respect to the font wave, the obtained time-of-flights values have to be corrected for diffraction effects. Today available analytical models, taking into account these effects, are based on the assumption that emitted wave is periodic and continuous, even if, for practical reasons, waves packet are formed by a limited number of cycles (usually sinusoidal signal bursts of 5-10 cycles). Unfortunately, in this way, analytical models can be considered just as a preliminary approximation of the real effects; thus, precautionary, the corrections are calculated and applied checking that their contribution is much smaller than that one of other uncertainty sources. For many industrial fluids this approach is reasonable, but for those of scientific interest it is not always acceptable. Furthermore, although measurement cells are designed to work in the far-field conditions, it could be happen that, for particular thermodynamics states, the measurements are obtained in near-field region where complex interferences can perturb the signal, leading to incorrect results. In this work, an original and time-dependent function is used in order to better approximate Reyleigh-Sommerfeld integral by a simple numerical algorithm. Using this theoretical approach, it is possible to calculate time-dependent acoustic field both in the near- and far-field conditions, and to use these results to correct experimental time-of-flight measurements. Examples including different geometrical parameters for the source and traveled distances are proposed in the case of speed-of-sound measurements in seawater sample.
A modulated quasi-adiabatic calorimeter has been realized for measuring specific heat capacity of fluids in a wide temperature range. The core of the thermostat consists of a 3 kg copper block set in a vacuum bell and thermally linked to a heat exchanger. System temperature is kept stable by a two stages control allowing to reach a temperature stability of about 0.5 mK. The measurement cell, equipped with an heater and a NTC-thermistor, is placed inside the core. The electric heater is excited by a millihertz modulated sinusoidal signal capable to induce a temperature oscillation of approximately 10 mK with an empty cell. The measurement of the amplitude of the oscillations is obtained by means of a lock-in amplifier in the case of evacuated cell, then with a reference fluid and finally with the sample. Measurements obtained using pure water, ethanol and toluene have showed a repeatability better than 10 part per million and an uncertainty typically better than 0.5%. Perspectives to use the instrument even for high pressure measurements and for measuring fluids thermal conductivity are illustrated.
Novel Experimental Methods to Quantify the Adsorption Thickness of Ionic Surfactant at Hydrophilic-Hydrophobic Interfaces

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In conventional energy production, the stability of liquid water or gas hydrate dispersions in the continuous hydrocarbon phase is determined by the energy bound at the hydrophilic-hydrophobic interface. Depending on the system’s chemistry, surfactants may be injected into the production system to manipulate or minimise this free energy and improve the ability of the system to flow. Conventionally, the performance of these surfactants is validated qualitatively through single-concentration interfacial tension or emulsion stability measurements. In this study, we used two experimental methods to quantify the competition between surfactants at hydrophilic-hydrophobic interfaces. First, pendant drop interfacial tensiometry (IFT) was adapted to quantify a matrix of adsorbed surfactant densities via Gibbs isotherm analysis. Ionic surfactants were studied over ten orders of magnitude in concentration. The results illustrate that ionic surfactants with similar molecular weight compete for adsorption sites at the water-oil interface, resulting in a decrease in overall packing efficiency below the critical micelle concentration. Second, Raman spectroscopy methods were adapted to quantify the extent of surfactant adsorption at the gas hydrate-oil interface above the dissolved concentration in the continuous phase. Together, these experimental methods can be used to develop structure-function maps for the development of future pipeline injection chemicals.
The 3ω measurement method is now widely used for thermal properties characterizations. The freestanding sensor based on polyimide film expands its application to much broader field, porous material, for example. Due to the existence of the polyimide film, the signal frequency must be low enough to ensure that it can penetrate the film and finally reach the sample. Lower frequency signal means larger time constant for the lock-in amplifier, thus the whole measurement process is time-consuming. In order to fundamentally reduce this time, new basement material for the freestanding sensor must be employed to increase the detection frequency and decrease the time constant. We choose sapphire as the basement for its high thermal diffusivity (more than one hundred times larger than the polyimide film), which is essential to determine the penetration frequency. Moreover, sapphire is rigid enough (which hardness is second only to diamond in nature) to resist most damage to the nickel strip deposited on it. A series of standard samples are tested by the new sensor, and results show that the stethoscope style freestanding 3ω technique make the measurement more rapid, and the sensor itself is more durable. Benefited from the reduction of measuring time, this technique achieves on-site measurement for the 3ω method, which means that thermal properties of most types of materials can be acquired easily, and the measurement process is no longer limited in laboratory.
Surface Tension of Nano-Confined Lattice Polymers

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Surface tension at solid/liquid interface is a key concept in understanding many important surface and interfacial phenomena such as wetting and capillarity. It is, however, not trivial to accurately calculate surface tension in lattice Monte Carlo (LMC) simulations, which are much faster than simulations in continuum. Here we propose a novel, efficient, and accurate method for calculating the surface tension of polymers confined between two parallel and impenetrable surfaces in LMC simulations, and examine how surface tension varies with the degree of confinement (i.e., separation distance between the two surfaces). Direct comparisons between our LMC results and the corresponding lattice self-consistent field (LSCF) calculations also unambiguously and quantitatively reveal the fluctuation/correlation effects on surface tension neglected in LSCF theory.
The uranium dioxide is the most used oxide as nuclear fuel due to many advantages such as: high stability even when it is in contact with water in high temperatures, high fusion point, and high capacity to retain fission products. The conventional fuel for pressurized water reactor with UO₂ ceramic sintered pellets stacked inside fuel rods, and presents disadvantages because its low thermal conductivity causes large and dangerous temperature gradients. The research project entitled "Beryllium Project" under development at CDTN (Centro de Desenvolvimento da Tecnologia Nuclear/Comissão Nacional de Energia Nuclear, Belo Horizonte, Minas Gerais, Brazil) aims the obtaining of fuel pellets made from a mixture of uranium dioxide microspheres and beryllium oxide powder to increase the thermal conductivity of the fuel pellets. This type of fuel promises to be safer than current fuels, improving the performance of the reactor, in addition to last longer, resulting in great savings. Increase in the thermal conductivity in the range of 8.6% to 125%, depending on the level of addition employed in the range of 1% to 14% by weight of beryllium oxide, has been obtained. In this work, a mixture of uranium dioxide kernels produced at CDTN’s nuclear fuel laboratories using the Nukem’s sol-gel process with 2 weigh percent of beryllium oxide was pressed into pellets. The pelletizing parameters and the thermophysical properties (density, thermal diffusivity and thermal conductivity) results are reported and compared with the values of the conventional uranium dioxide nuclear fuel.
A High Resolution Thermal Mapping of SF$_6$ Fluid Near Its Criticality in Weightlessness

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Early stage of thermal equilibration near the liquid-gas critical point of fluid sample in a constant volume cell is rapid due to the adiabatic process, called “piston effect.” Nevertheless, the later stage of the equilibration is governed by the slow diffusive process. Therefore the complete equilibration process depends on the thermal performance of the regulation system, and then of the sample cell material, its geometry, thermophysical properties of the sample fluid, and the thermal history of the sample. Experiments to study the critical phenomena extremely close to the critical point have been hampered by the resulting residual temperature gradient and its associated local density inhomogeneity. Even for a high quality level thermal regulation, this residual temperature inhomogeneity inside the fluid can be extremely small near the critical point and not measurable directly using a conventional thermometry. Here we show indirect measurements of two dimensional temperature and density profile of near critical SF$_6$ fluid in an entire cylindrical cell by a wide field-of-view turbidity measurements and a theoretical equation-of-state model. This turbidity measurement was performed in weightless conditions using the DECLIC (Dispositif pour l’Etude de la Croissance et des Liquides Critiques) facility and the ALI insert on board International Space Station (ISS). We will present the new thermal mapping technique for a near critical fluid and its applications to study critical phenomena.
Experimental Determination of \((p, \rho, T)\) Data for Binary Mixtures of Methane and Helium

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Experimental characterization of the thermodynamic behavior of gas binary mixtures containing components of fuel gases is of great importance due to the proved lack of reliable data of thermodynamic properties of mixtures. These data are essential not only for the improvement and test of the current reference equation of state for natural gases and related mixtures, GERG-2008, but also for the indirect determination of other properties. GERG-2008 equation of state is based on formulations developed for 21 pure components and for the binary mixtures of these components. Due to the lack of experimental data for binary mixtures, and to the complexity of the process, most of the binary systems were taken into account by using adjusted reducing functions for density and temperature. Only for those binary mixtures for which sufficient accurate experimental data were available, binary specific departure functions or a generalized departure function were developed. For the binary mixture methane-helium no departure function was developed. In this work density measurements for three binary mixtures of methane with helium are presented. Therefore, accurate density measurements for binary mixtures of methane with helium \((x_{\text{He}} = 0.05, 0.10, 0.50)\) are performed at temperatures between 250 K and 400 K, and pressures up to 20 MPa, using a single sinker densimeter with magnetic suspension coupling, which is one of the state of the art methods for density determination over wide ranges of temperature and pressure.
Experimental Determination of the Density of Two Synthetic Natural Gas Type Mixtures

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Experimental characterization of the thermodynamic behavior of multicomponent gas mixtures of accurately known composition is of great importance for testing the current reference equation of state for natural gases and related mixtures, GERG-2008. Natural gas composition may change considerably due to the diversity of origins, or the possibility to incorporate hydrogen, biogas or other non-conventional energy gases. In this work density measurements for a synthetic hydrogen-enriched natural gas mixture (13 components, xH₂ = 0.03) and for a synthetic natural gas with a composition similar to a typical liquefied natural gas (9 components), are presented. Both mixtures were prepared gravimetrically. Accurate density measurements are performed at temperatures between 250 K and 400 K, and pressures up to 20 MPa, using a single sinker densimeter with magnetic suspension coupling, which is one of the state of the art methods for density determination over wide ranges of temperature and pressure.
Water Density Measurements in the Temperature Range of (243 and 273) K and Pressures up to 400 MPa

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Although pure water is probably the most studied fluid, there are regions of the phase diagram, at high pressure and low temperature, where thermodynamic properties are still lacking of the needed accuracy. Thus, a pseudo-isochoric method, consisting of a high pressure vessel with an expansion cell, has been realized in order to measure the density of pure water in the temperature range of (243 to 273) K and for pressures between (200 and 400) MPa. Exploiting the expansion cell, mass of the sample is determined at pressure lower than 10 MPa, by means of IAPWS-95 density reference values. The experimental apparatus has been characterized and tested in the temperature range of (278.15 and 343.15) K and at pressures up to 100 MPa, in order to determine the volume of the pressure vessel. Furthermore, the corrections to the volume for the effect of temperature and pressure variations have been considered. The density of subcooled water has been obtained by measuring the pressure as the temperature changes, at constant mass. Terms contributing to the uncertainty in determining the volume and the mass have been considered to obtain a final uncertainty of subcooled water density better than 0.2%.
Lindemann’s criterion of melting is utilized to develop the empirical equation of state to estimate the melting curves at high pressure for NaCl, KCl, RbCl, NaBr, KBr, CsBr, NaI, KI, CsI, LiF, NaF and KF. The solid-liquid phase transition i.e. melting of halides at high pressure is of considerable significance to understand the structural phase transformation and the information regarding the role played by thermodynamic functions. In particular, the molten salt phase diagrams are of central importance in metallurgy and material science due to their industrial applications. The basic inputs for our formulation are the bulk modulus and the Grüneisen parameter at the ambient conditions. Under simple conditions, the present formalism reduces to the well-known Simon’s relation. Most of the melting curves (T_m-P) exhibit nonlinear variation with increasing pressure having curvatures downwards. Contrary to this, T_m-P melting curves of CsBr and LiF show nonlinear variation with curvatures upwards. The gradients, dT/dP are found to be quite different for different halides. The computed curves of Tm-P variation are in very good agreement with the available experimental data.
This work is done in frame of EMRP project SIB10 NOTED “Novel techniques for traceable temperature dissemination”. One activity of this project is improving the current realisation of the international temperature scale (ITS-90) by a systematic study of the uncertainties in the realization of the defining fixed points due to impurities in the fixed point materials. Phase diagrams for low impurities concentration in the fixed point material do not currently exist, so it is not possible to perform any corrections due to impurities in the fixed point temperatures. Work aims to precisely quantify the temperature effect of some common impurities in the defining metal fixed points (gallium and aluminum). The uncertainties due to impurities correspond, on average, to about 20 % of the total uncertainty. In this paper will be presented the results of doping experiments in Ga and Al cells with Pb and Ni at 2 different concentrations obtaining their corresponding phase diagrams. Second part of the paper will deal with a metrological assessment of melting and freezing plateau and give the uncertainty estimation of these measurements.
Diffusion of Heat and Mass in a Chemically Reacting Mixture

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We report transport properties for the hydrogen dissociation reaction driven by a thermal force, at conditions where reactants and product concentrations are both sizable. The data are obtained for the first time from non-equilibrium molecular dynamics simulations of reactions far from chemical equilibrium. The results derived from the system’s entropy production, show that the strongly endothermic reaction has a large impact on the transport coefficients. The thermal conductivity was found to be comparable to that of a medium dense gas at high temperature (1 W/mK), while the observed diffusion coefficient was small ($10^{-7}$ m$^2$/s). The coupling coefficient as expressed by the heat of transfer is was found to be in the same order of magnitude as earlier studies. This is at variance with the common perception that the Dufour effect is negligible in reacting mixtures.
The speed of sound of two (argon + carbon dioxide) mixtures was measured over the temperature range of (275 to 500) K with pressures up to 8 MPa utilizing the spherical resonator system of the National Institute of Standards and Technology. The compositions of the gravimetrically prepared mixtures were (0.50104 and 0.74981) mole fraction carbon dioxide. The measurements were carried out to improve the data basis for binary mixtures relevant for carbon capture and storage (CCS). It is known that the vibrational relaxation of pure carbon dioxide is distinct and leads to high sound absorption at frequencies of the order of 10 kHz. This circumstance significantly impedes the sound speed measurements on carbon dioxide and its mixtures. In contrast to the standard operating procedure for the spherical resonator, non-radial resonances at lower frequencies had to be taken into account. Still, the data show a comparatively high scatter and the usual overall uncertainty of this general type of instrument could not be matched with the present measurements. However, the results are compared to the GERG-2008 reference equation of state for natural gas and to a Helmholtz energy model specifically fitted for humid gases and CCS mixtures. The recent experimental data will be useful for improving the interaction parameters in equations of state describing CO₂-rich mixtures. To extend the work on sound speed measurements on CO₂-rich binary mixtures, a new spherical resonator system has been set up at the Thermodynamics Institute of Ruhr-University Bochum. We also present first results from measurements with this new instrument.
We present here pressure dependence of the thermal and physical properties of titanium oxide (rutile) using a semi-empirical approach based on Lindemann’s melting law. Rutile is the most common naturally occurring and most stable polymorph of titanium oxide (TiO₂) with a tetragonal symmetry. The amount of rutile found in nature ranges between 0.5% and 0.8% of the total mass of the Earth’s crust. It is used in photovoltaic devices, integrated wave guides, gas and humidity sensors, and solar cells. Research on rutile is important to earth scientists because a complete understanding of the composition and thermal state of the Earth’s interior depends on information about the elastic properties of this mineral at high pressure and temperature. We have used semi-empirical equations to determine the melting temperature, $T_m$ and Debye temperature, and their pressure dependence. The formalism used to compute $T_m$ is based on Lindemann’s melting law. In both the cases we have assumed linear dependence of bulk modulus, $B$ and Grüneisen parameter, $\xi$ on pressure. We have applied the formalism to estimate the pressure dependence of viscosity, diffusivity and conductivity of rutile (Titanium oxide, TiO₂). These results show that the pattern of the pressure variation of melting temperature influences the pressure dependence of viscosity, diffusivity and thermal conductivity. The pressure range used in the present study is 0-50GPa. Our analysis shows that the maximum and $T_m$ and maximum $\Theta_D$ of rutile are 2695K and 967K at 43GPa and 51.2GPa respectively indicating possible mineralogical phase changes. Viscosity, diffusivity and thermal conductivity at zero pressure and melting temperature are 2.95mPa.s, $4.78 \times 10^{-5}$cm².s⁻¹ and 7.23 W.m⁻¹.K⁻¹ respectively.
The transport of carbon dioxide (CO₂) between the capture and storage point is matter of great importance for the oil and gas industry, although it is not as often debated. NOV (National Oilwell Varco) manufacture flexible pipelines for offshore transport of fluids in deep water conditions. Flexible pipelines become a good alternative to the rigid ones, mainly because of the following advantages: easier storage and transport, lower operating costs, simpler maintenance and higher chemical and mechanical resistance. A flexible pipeline consists in several layers, where the so-called inner polymer liner provides the barrier to the egress of the gas being transported. Inside the pipeline the gas is transported at extreme conditions of temperature and pressure, within the range of the supercritical stage (e.g. 90 °C and 650 bar). The study and optimization of these pipelines systems is an experimental challenge that requires the acquisition of some thermodynamics and transport properties of supercritical gases: solubility and permeability of the polymer/gas system at as function of pressure and temperature. In this work, two different apparatus systems are used to test determine the key properties of the gas/polymer system: a Magnetic Suspension Balance (MSB), to determine the solubility, and a 2-D permeation cell, to measure the permeability. The measurements were performed with three different polymers, PVDF, XLPE and PA11, while using pure CO₂ and its mixture with methane (90/10) at different conditions of pressure and temperature. These results, obtained under collaboration with NOV as industrial partner, have direct impact in the safety and operating conditions of gas transport in flexible pipelines.

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The applications and importance of prediction of solubility of organic molecules spans across a large sector of the chemical and pharmaceutical industries. The diverse and wide range of molecules for which such predictions are needed also have a wide range of other physicochemical properties. A successful method to predict solubility of solutes in solvents for such a variety of compounds needs to be very versatile in terms of the types of molecules it can describe, while being accurate over broad ranges of conditions. Group contribution approaches can be very powerful techniques in this context. In the SAFT-$\gamma$ Mie group-contribution approach [1] a heteronuclear model is implemented and an accurate expression for the Helmholtz free energy change due to association is obtained for pure components. The physicochemical properties of molecules of interest are described by appropriate summation of the contributions of the groups they contain. Each of the groups is characterised based on the fluid phase behaviour and properties of simple molecules, and the parameters characterizing the groups are then transferred to more-complex molecules. The robustness of the underlying physics allows the treatment of a broad collection of compounds, including associating ones, and provides the ability to describe a wide array of physicochemical properties with a single set of interactions. Although the group-contribution method enables many molecules to be treated with a small number of constituting groups, the power of the approach is truly demonstrated when the solubility of large and complex multifunctional pharmaceutical molecules is predicted based only on experimental data that were obtained for small and simple molecules. Here we provide a wide range of examples of the prediction of solubility of organic molecules ranging from asymmetric alkanes mixtures to lovastatin in various solvents.

References

Thermophysical Properties of Poly(2-hydroxyethyl methacrylate) Hydrogels as a Methane Storage Material

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Poly(2-hydroxyethyl methacrylate) (PHEMA), a synthetic crosslinked hydrogel, with outstanding ability to absorb and retain a high water content and still maintain their solid state, has been studied as scaffold for methane gas hydrates. The high water content, excellent hydrophilicity and interconnected pores of these hydrogels could be ideal to support the methane hydrate formation and to enhance gas permeation and interactions with water molecules. The heat released during the formation of per kilogram of methane hydrate is as much as 438.54±13.78 kJ. Whether the heat can be removed from the hydrate-hydrogel system in time is critical to the formation of methane gas hydrates. In this work, thermal conductivity is investigated for different temperatures and monomer contents to better understand thermal behaviors of PHEMA hydrogel during the hydrate formation process. Several theoretical models were applied to calculate hydrogel’s thermal conductivity and the prediction results were compared with experimental values. Results were found that thermal conductivity strongly depends on monomer content and ambient temperature. With monomer content ranging from 100 wt% to 5 wt%, thermal conductivity can increase from 0.13 W/(m·K) to 0.59 W/(m·K). At some point below 273 K, the thermal conductivity of all hydrogel samples experiences a sudden rise to around 1.50 W/(m·K), about 200% larger. Other thermophysical properties like heat capacity and thermal stability were also investigated using differential scanning calorimetry and thermogravimetric analysis respectively.
The transient hot wire technique is suitable for measurement of heat conductivity of simple and complex fluids. This technique is used to measure thermal conductivity of gases, organic liquids, electrical non-conducting and conductor liquids. Furthermore, it is possible to achieve a precision of 0.1 to 0.3 % and uncertainties from 0.3 to 0.5 %. To implement this technique in the Centro Nacional de Metrología (CENAM) of Mexico it was realized a design of a measuring system for both simple and complex fluids. In this technique a Pt-wire is immersed in the fluid of interest. When an electrical current passes through the wire heat is dissipated by Joule effect. Once the wire is energized its temperature tends to a steady value. The key feature of this technique is to measure the wire temperature during the transient time between the initial temperature and the steady state condition. The heat rate transfer from the wire to the fluid depends on the thermal conductivity of this one. On the other hand the heat transfer is expected to be only by conduction, thus radiation and convection effects should be minimized by design. The cell design is such that for a short time of measurement (of the order of 1 second) convection is negligible and it is not present in the heat transfer phenomena, in that time the measuring system should be able to collect enough data to evaluate the thermal conductivity. We present the operational tests.
Molecular Dynamics Calculations of Intermediate Scattering Functions for Colloidal Fluids in Explicit Solvent

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Unimodal and bimodal colloidal suspensions are extremely useful model systems for the study of nucleation and vitrification. As the packing fraction of a unimodal colloidal solution is increased beyond the melting point, it crystallizes into a solid. But for the bimodal solution, polydispersity inhibits crystallization and therefore promotes a glass transition, where the system undergoes a transition to an amorphous solid [1]. Because of the convenient size and time scales of colloidal suspensions, colloidal crystallization can be studied using light scattering and microscopy [e.g. 1-3]. One of the main properties measured by light scattering is the intermediate scattering function (ISF) [e.g. 3], which is the auto-correlation function of the density-density fluctuations. Molecular Dynamics (MD) simulations of hard-sphere (HS) systems [e.g. 4], have been performed to provide a comparison with experiments, but to date none have taken into account hydrodynamic interactions (which are present in real colloidal systems) by simulating the solvent explicitly. We have used MD simulations with explicit solvent, to conduct a systematic study of the ISFs for both unimodal and bimodal colloidal suspensions near the melting point and in the metastable region. The aim of this study is to reveal new quantitative information about the causes of metastability, providing a better understanding of the processes that inhibit crystal formation and promote the glass transition.

References

A New Fundamental Equation of State for Heavy Water

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Many engineering applications such as simulation, control, and evaluation of processes in energy technologies demand extensive knowledge about the thermodynamic properties of the involved fluids. Nowadays, the most accurate way to determine these properties is by means of empirical multiparameter equations of state. In this work, a new fundamental equation of state for the thermodynamic properties of heavy water was developed. Since its discovery in the early 1930’s, heavy water has been of significant industrial interest, especially in nuclear power cycles. Aside from this application, it is scientifically important as a source of information about the isotopic impacts on thermophysical properties. The current reference equation of state for heavy water was published by Hill et al. (1982). In comparison to modern formulations for other fluids, this equation has an unnecessarily complex functional form with a total of 50 terms. Due to advances in the development of equations of state and modern computer technology, it is now possible to develop an equation with fewer parameters without loss of accuracy. The new equation is explicit in the reduced Helmholtz energy with density and temperature as independent variables. Compared to the formulation by Hill et al. (1982), the new equation of state contains less than half the number of terms. It describes the whole fluid region for temperatures and pressures up to $T = 825$ K and $p = 1200$ MPa. The accuracy of the equation was validated by comparisons to the available experimental data. Based on an evaluation of properties at extreme conditions of temperature and pressure, the extrapolation behavior of the equation was found to be reasonable. The new formulation will be proposed as a standard for adoption by the International Association for the Properties of Water and Steam (IAPWS).
Due to increased computer performance, recent progress in molecular models (force fields) and its simulation methods, simulated thermodynamic data have already been used to extend experimental data sets to develop fundamental equations of state (FEOS) [1-2]. However, the accuracy of the simulated thermodynamic properties is limited by the quality of the underlying molecular model. The common standard of optimizing molecular models nowadays only considers vapor-liquid equilibrium data \((p_v, \rho', h_{vap})\). The presented optimized potential model (PM) for CO2 is based on the rigid model published by Merker et al. [3]. New potential parameters were optimized to thermodynamic properties in the homogenous fluid region as well as to vapor-liquid-equilibrium (VLE) data. CO2 was considered because its fluid region is described by the highly accurate reference FEOS of Span and Wagner [4]. The experimental data available for CO2 are generally reproduced by this FEOS within their experimental uncertainty. Therefore, the FEOS was used to generate the property data required to optimize the PM. The iterative optimization procedure uses parameter variations of the original model. When a parameter of a PM is varied by a small magnitude, a shift in the thermophysical properties from the parameter variation can be observed. By changing all parameters of the model, one at a time, a system of equations can be set up to solve the minimization problem. After the optimization, the accuracy of the PM was significantly improved for saturated liquid density and vapor pressure. In the homogenous region, the accuracy of the isochoric heat capacity and speed of sound was improved. The representation of other thermodynamic properties remained nearly unchanged. Finally, the limitations of the optimization method were investigated. It was shown that simultaneous optimization of the PM using homogeneous and VLE data is difficult, which may be due to simplified nature of the PM.

References

Simultaneous speed of sound and density measurements, together with data of other complementary quantities (such as temperature and pressure) are of great importance to obtain an enhanced characterization of unknown fluids thermodynamic state or their contaminations. Differently from commercial ultrasonic densitometers, here proposed sensor has been designed to obtain independent density and speed of sound results and to be totally immersed into the fluid. In practice, a speed of sound sensor has been adapted to support an additional piezoelectric transducer, which is coupled to the cell by means of a buffer rod. In this configuration, it is possible to obtain the density, \( \rho \), of a liquid sample by measuring its acoustic impedance, \( Z \), and the sound velocity, \( w \), (\( \rho = Z/w \)). The newly designed sensor has been calibrated with pure water and tested using \( n \)-nonane in the temperature range between (258.15 – 318.15) K and for pressures up to 30 MPa. The obtained results have been compared with the literature values and the relative uncertainty is better than 0.2 % for both density and speed of sound.
Compressed-liquid densities of three compositions of the binary mixture dimethyl ether + pentane have been measured with a vibrating U-tube densimeter. Measurements were made from 270 K to 390 K and 1.0 MPa to 50 MPa. The overall combined uncertainty (k=2) of the density data is 0.81 kg·m⁻³. Data presented here have been used to improve a previously formulated Helmholtz energy equation of state. The newly derived parameters are given. The polar + non-polar nature of the dimethyl ether + pentane system presents modeling challenges. The interactions of such pairs are often more different than straight-chain hydrocarbon pairs upon which many equations of state base their mixing parameters. The compressed-liquid density measurements presented in this work were thus undertaken to provide non-saturation data for the dimethyl ether + pentane system with the goal of developing an equation to more accurately predict thermophysical properties for this mixture. Additionally, the data serve for further improvement of equations of state in predicting the properties of mixtures that include polar + non-polar interactions.
Determining Saturation Curves through Oscillating U-tube Density Measurements

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Thermodynamically, as a pure fluid held at a constant temperature transitions (through a loss or increase in system pressure) from the compressed-liquid state into the two-phase vapor-liquid state or vice versa, there is an abrupt change in the fluid density. The purpose of this instrument development was to explore if that density change could be measured quickly and repeatedly with careful modifications made to a commercial oscillating U-tube density meter. The details of the apparatus will be presented and the pure fluid data discussed.
Fundamental Equation of State of Octafluoropropane

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In this paper, an octafluoropropane fundamental equation of state (EOS) developed on the basis of the Helmholtz free energy. The expression for this EOS is obtained on the basis of the phenomenological theory of critical phenomena [1] and the hypothesis of the same nature of the behavior of the isochoric heat capacity, isothermal compressibility and isobaric heat capacity for critical and near-critical isochores [2]. Non-analytic EOS describes the neighborhood of the critical point in accordance with the scaling theory of critical phenomena. Based on the proposed EOS calculated table of octafluoropropane thermodynamic properties on the phase equilibrium in the temperature range from the triple point to the critical point. In the single-phase region table are calculated in the temperature range from 125.45 K to 460 K and pressures from 0.001 to 70 MPa including a wide neighborhood of the critical point. It has been shown that the deviation calculated by the EOS of this work and the experimental density values in the temperature range from 130K to 210 K in the liquid region in the wide neighborhood of the critical points lie between 0.05% and 4%, respectively. Calculations using the EOS [3] showed that these variations are within 1.5% and 35%, respectively. Standard deviation calculated by the EOS of this work and the experimental data were: density in the single-phase region 0.32%; isochoric heat capacity including a wide neighborhood of the critical point 0.6%; density on the liquid branch of the saturation line 0.14%; the density of the vapor branch line saturation 0.7%; “apparent” heat of vaporization including the near critical region 0.38%; the heat capacity of saturated liquid 1.1%, isobaric heat capacity 2.4%.

References
The immense importance of vapor/liquid equilibrium in industrial processes has been extensively studied for several decades. The description of how molecules distribute themselves in an equilibrium system is important for chemists, physicists, and chemical engineers on a daily basis. In this work, we describe the equilibrium between a liquid-like and vapor-like phase of benzene in a microporous material, a system with three-dimensional cages on a molecular scale (MOF-5). The two-phase equilibrium has been studied using computer simulations as well as NMR relaxation measurements. Both of these techniques confirm the two phases are on a length scale significantly longer than the characteristic size of the pores. Previously, two-phase equilibrium has been thought impossible in such a nanoporous material. However, with a sufficiently open structure, the interactions between neighboring cages allow for interactions between guest-molecules, thereby lowering the critical point. At sufficiently high temperatures, the two phases transition into a single critical phase. Using computer simulations, we have described a phase-diagram for benzene in MOF-5. This phase-diagram is comparable to the phase-diagram seen for bulk-systems, but with a significant lowering of the critical point. By systematically changing the pore size, the critical point can be lowered from the bulk-phase critical point, and for very small cage sizes, the critical point disappears completely. This transition from two-phases to a super-critical phase has been verified experimentally, and is in good agreement with the simulation data for this system.
We examined the structure of water near a calcite surface using different force fields to describe the interaction between water and calcite. While the majority of potentials used to model water-calcite interactions in atomistic simulations have been derived from dedicated fitting investigations aiming to match experimental properties of water in contact with surface [1, 2], our goal was to formulate a more general technique based on “same-atom” Lennard-Jones or exponential-six form potentials. Our potential-fitting procedure was based on potential splitting due to Weeks-Chandler-Andersen approach [3], with Barker-Henderson integration [4] employed to estimate the effective hard-sphere diameter. This procedure keeps the partial charges unchanged, and utilizes standard combination rules to determine the values of temperature-dependent hard-sphere diameter, well depth, and area under the curve to be matched by the cross-term potentials. The ultimate goal of this approach is to apply this methodology to molecular dynamic simulations of aqueous water systems to generate cross terms for solute species in cases where no pre-existing interaction potentials are available either from matching experimental results or ab initio studies. To validate the fitting procedure, we compared water structuring in an interfacial system composed of water and a slab of calcite measuring roughly 45Åx40Åx50Å. Tested force fields included those obtained from fitting Buckingham same-atom water and calcite as calculated in [5], water-calcite potential directly due to [6], and TIP4P-Ew water [7] – calcite cross terms of [1]. The location and the relative height of water density peaks in the vicinity of calcite agreed very well in case of parameters derived from fitting procedure and the force-field due to [5, 6], thus being closer to its experimental position of 2.5 Å in [8]. The structure of double-layered adsorbed water combined distinctive features of hydrated calcite surfaces in Gale et al [9] and Perry et al [10].

References


During the remaining 100 years or so, there are concerns regarding the drain on the current major primary energy sources of oil, coal, natural gas and uranium. Therefore, utilization of renewable energy in order to reduce the use of limited resources has attracted attention. We have focused on geothermal energy, which a renewable energy source. For the design of a Ground Source Heat Pump (GSHP) system, it is important to understand the thermophysical properties of the soil. GSHP commonly uses the heat energy of soil approximately 100 m underground, however expensive drilling costs (about 10,000 Yen/m) prohibit the progress of the GSHP system in Japan. Furthermore, geology in Japan makes it difficult to design a suitable GSHP system. In this study, we have focused on the development of a ground source heat pump system with pile heat exchangers for a residence (GSHP with PHEs). A pile heat exchangers has 20 or shorter. Heat flow in the ground is 2 dimensional because pile heat exchangers are short. So, Thermal Response Test method is not applicable to know the thermal properties of the soil. In order to develop such a GSHP system, understanding of the thermophysical properties of the soil must be incorporated into the measurement system. Therefore, we measured the thermophysical properties of the shallow soil, approximately 10 m underground. A pile serving as a heater and a temperature sensor was set up in the soil; the pile was heated and the subsequent temperature rise was measured. The thermophysical properties such as thermal conductivity, specific heat and density were then estimated by fitting experimental data with numerical analysis based upon the principles of unsteady heat conduction.
Accurate vapor-liquid phase equilibrium measurements are performed on the binary CO$_2$-O$_2$ system using a setup specifically designed for CO$_2$-rich mixtures and conditions relevant for CCS transport and conditioning employing an analytical technique. Preliminary experiments show that the measurements can be done with low standard (k=1) uncertainty, within 10 mK in temperature, 0.05 percent in pressure, and 0.1 percentage-points in composition. The setup has been specifically designed to compensate for pressure drops caused by removal of a composition sample from the equilibrium cell, enabling the possibility of several composition samples at the same pressure close to the critical point at a certain temperature. According to recently reported comprehensive literature studies, experimental vapor-liquid equilibrium data for this system are scarce, and of varying quality. For instance, some of the seemingly most accurate available vapor-liquid equilibrium data for the CO$_2$-O$_2$ system are not consistent with the vapor pressure of pure CO$_2$, hence indicating an error in the pressure measurements of these data. The objectives of the current measurements are to reconcile the inconsistencies in the available literature data and to otherwise cover gaps in the available data including states close to critical conditions and temperatures above 273.15 K, where little data of sufficient quality exists. Measurements will be reported for several isotherms from 223.15 K up to close to the critical temperature of CO$_2$, with the possibility of carrying out experiments at pressures from 0.4 MPa to 20 MPa, and comparison with existing data and models will be provided.
Modern high performance aircraft commonly use the fuel as not only a propellant, but also a heat transfer fluid, hydraulic fluid and even a lubricant. Indeed, in the near future, lubricating subsystems will be completely eliminated from high performance aircraft. Thus, the fuel will be expected to fulfill the lubricant role flawlessly. To enable this transition, we are measuring a suite of properties for lubricant base fluids and mixtures, with the goal of defining the molecular characteristics of lubrication. In this talk the first series of measurements will be presented. This will include the chemical characterization and thermal decomposition kinetics for a series of polyolester lubricant base fluids, as well as one fully qualified formulation that incorporates all additives. The chemical characterization was done by gas chromatography coupled with mass spectrometry, tandem mass spectrometry, and flame ionization detection. The thermal decomposition kinetics were measured by the ampoule reactor method introduced at NIST for complex fluids.
Development of a Helmholtz Energy Based Empirical Model for Thermodynamic Properties of Ethanol-Oil Mixtures

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The knowledge of thermodynamic properties of fluids and fluid mixtures is necessary for the development of technical ORC processes. Nevertheless it is a common standard to design ORC processes using only the working fluid equations, whereas in many applications there is a relevant amount of oil involved. This approach is caused by a lack of knowledge for describing such complex mixtures. The presented preliminary model makes it possible to consistently model mixtures of ethanol and a poly-alpha-olefin (PAO). In order to describe the PAO as a pure fluid, a Helmholtz equation has been fitted using the functional form developed by Alexandrov et al. [1]. This generalized form was fitted to many short and long chained hydrocarbons and leaves only the critical temperature and density as well as the acentric factor as parameters that can be specified. This approach was chosen since only very limited data are available for the oil. In order to model the binary mixture, the reference equation for ethanol by Schroeder et al. [2] has been used. The new empirical mixture model was formulated in terms of the Helmholtz energy. Only limited phase equilibria data are available in a temperature range from 413 K to 453 K. The model qualitatively reproduces the vapor-liquid equilibria of this complex mixture. Furthermore, it seems feasible to also qualitatively represent mixtures of R134a or CO₂ and the PAO with this approach, although there is no accurate data available for the validation of these systems.

References

Emissivity of the Mg$_{49}$Zn$_{51}$ Alloy: a Candidate for Thermal Energy Storage

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Among different kinds of materials, metals and alloys have been proposed as potential candidates as phase change materials (PCM) for thermal energy storage (TES) systems in concentrated solar power (CSP) plants. The eutectic Mg$_{49}$Zn$_{51}$ alloy seems to be a good PCM candidate since it has an adequate melting point temperature and good specific heat and thermal conductivity values. In order to calculate the thermal heat losses, the radiative properties are studied in this work. Two different emissivity measurement sequences are performed in an inert atmosphere. One of them to observe the phase transitions below the melting point through time dependent measurements at constant temperature. The other is the usual emissivity plot temperature between 200 and 300 °C. Below the eutectic temperature (341 °C) a second order phase transition is observed (327 °C) and its enthalpy must also be taken into account in the thermal energy storage. This phase transition is observed and studied by using spectral emissivity measurements and calculating the total emissivity values. Radiometric measurements are also made in a normal atmosphere in order to observe whether there is any kind of oxidation or not and determine if an inert atmosphere is necessary in a thermal energy storage system.
Heat Capacity Measurements of Aviation Turbine Fuels

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Petroleum refinery operations and related processes require knowledge of heat capacity data over a wide range of temperatures. For example, heat capacity data are instrumental to the design of plant equipment, as well as to process decisions related to issues such as prolonged storage or low temperature operability. Furthermore, heat capacity can be used to evaluate other basic thermodynamic properties of a fuel. In this work, specific heat capacity has been measured for seven aviation turbine fuel samples: Jet A, Jet A-1, JP-4, JP-5, JP-7, JP-8, and JP-10. All measurements were made using modulated differential scanning calorimetry over the combined temperature range of 223 to 453 K. Experimental data, including an assessment of the associated expanded uncertainties, will be presented. Additionally, measurement results will be compared to available literature data and to existing surrogate mixture models.
The DIPPR 801 Gold Standard Systems Approach to Critical Evaluation of Thermophysical Property Data

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Accurate, pure-chemical, thermophysical property data are an essential component of designing and optimizing chemical processes, but the literature is filled with conflicting information and incorrect values. Using inaccurate data can be expensive. For example, an error of 10% in liquid heat capacity can result in thousands of dollars in unanticipated heating costs annually for a single medium-sized heat exchanger. To combat inconsistent literature, the DIPPR database uses a systems approach to evaluate the data from all available sources and triangulate on the best values. This approach applies over one hundred constraints—including inter-property relationships, expected trends between related chemicals, and chemical similarities and differences—to produce higher accuracy than could be achieved using only individual points or an evaluation approach which applies only a few consistency checks. Once the constraints are simultaneously satisfied for all properties, experts manually review the compound prior to addition to the database as a final quality check. This presentation will explain the systems approach to critical evaluation in more detail, and how this fits into DIPPR’s mission to be the gold standard database in terms of both accuracy and completeness. Efforts to continuously improve the database, by developing new prediction methods and reevaluation of compounds already found in the database, will also be explained using two examples. The first is a description of a new method to predict liquid heat capacities from heat of vaporization, ideal gas heat capacity, and liquid vapor pressure using thermodynamic integration along the liquid-vapor saturation curve of a compound. The second is a recent reevaluation of the properties of the 1, \( n \)-alkanediol family of compounds. Taken as a whole, the results show the robustness of the systems approach to data evaluation, and how it provides insights into thermophysical property data that cannot be obtained using simpler methods.
Strategies to Stabilize Proteins on Surfaces from Improved Modeling of Protein-Surface Interactions

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The interaction of proteins with surfaces is a central phenomenon in many applications in medicine, biotechnology, and proteomics. Understanding protein/surface interactions is key to improving these technologies, but current understanding of the behavior of proteins on surfaces is lacking. One of the challenges is that little is known about the biophysics involved in protein-surface interactions. Traditional experimental techniques used to determine protein structure—NMR and X-ray crystallography—are bulk techniques that are not amenable to surface-bound proteins, so simulation has emerged as the primary method to investigate the relevant phenomena.

This talk explains how coarse-grain models have been developed and used to understand the thermodynamic stability of proteins on surfaces. We first show that by measuring stabilization using melting temperatures (obtained from heat capacity curves) and the Gibbs energies of folding, that the stability of small proteins tethered to surfaces can be correlated to the type of loop region where the tether is placed. We also show that any destabilization that occurs because of the surface is an enthalpic effect and that surfaces always stabilize proteins entropically.

Second, we show how surfaces can drastically change the folding behavior of proteins on surfaces and how selecting correct tether positions, including using multiple tethers, can remove unstable intermediates and improve stability of enzymes. Finally, we demonstrate a new coarse-grain, protein-surface model that overcomes many previous limitations and how this model has been extended to antibodies and antibody fragments. Results will be presented that show: 1) the thermal stability of antibodies and antibody fragments is mostly a function of surface type and is less dependent on the orientation of the immobilized molecule on the surface and 2) that surfaces destabilize antibody-antigen binding. As a whole, the results offer hope that rational design of technologies involving protein-surface interactions, including protein arrays, is possible.
Accurate thermodynamic property data of refrigerant are important to estimate and to evaluate HVAC&R applications performance. In recent years, high temperature heat pump systems have received a lot of attention, because they can generate hot water by using waste heat. On the other hand, refrigerant need to have lower environmental impact and to work at higher temperature. In this study, a set of PVT properties data in gas-phase region for a couple of fluoro-butenes are presented. Fluoro-buthene is one of the hydrofluorolefin (HFO) refrigerant. The environmental impact of HFO refrigerant is extremely low and the critical temperature is higher than that for refrigerant applied to refrigeration or air-conditioning. The experimental PVT properties of fluoro-buthene have been measured by a magnetic levitation densimeter (MLD). MLD is one of the most accurate measurement technique to measure density under high-pressure and high-temperature conditions. Density is measured by MLD with Archimedes' principle. The measurement procedure of MLD is two steps. At first, the sinker in the measurement cell with sample has filled floated by a magnetic force. Second, buoyancy measured by balance. Density calculated by sinker density and buoyancy. The sinker is made by silicon single crystal and that is calibrated. In this study, the apparatus was newly developed and measured Tetrafluoro-butenes density. A densimeter cell is thermostated by an aluminum block and a thermal shield placed in an evacuated chamber. Temperature is measured by a standard PRT placed inside the aluminum block. Pressure is directly measured by a quartz pressure transducer. The measurement range of temperature is from 340 K to 400 K, pressure up to 5 MPa, respectively. The experimental uncertainties of the present measurements are estimated to be within 0.02 K in temperature, 0.7 kPa in pressure, respectively.
We will provide fundamental thermophysical and chemical property data of important cannabis compounds (natural, synthetic, and endogenous cannabinoids) and their important metabolites. An ultra-sensitive, quantitative, trace headspace analysis technique called porous layered open tubular-cryoadsorption (PLOT-cryo) will be used to make thermodynamic measurements of the enthalpy of vaporization. This technique is based on traditional purge and trap methods that were designed for sampling volatile organic compounds prior to chromatographic analysis. We have modified the experimental approach dramatically to allow for facile and sensitive detection of low volatility and/or trace compounds. We have shown with previous work that this application is especially useful for precise quantitative analyses and analyses as a function of sample temperature. We will present this data in the form of a van’t Hoff equation plot, which will plot the concentrations as a function of headspace collection temperature. A linear relationship of the recovered mass as a function of inverse collection temperature will reveal the predictive capability of the methodology employed here. Additionally, we will determine the vapor pressure of several of the cannabinoids. Characterization of the thermophysical properties of these compounds will aid in vapor detection of cannabinoids and metabolites, aiding in the development of in-the-field vapor detection devices for law enforcement personnel to be able to detect recent drug abuse.
Correlations of the thermophysical properties of fluids still depend strongly on accurate measurements. For viscosity measurements, the vibrating wire viscometer has served as the main experimental method for decades. A rigid theory of the instrument was developed by Retsina et al. (1987) assuming point symmetry in the flow field to obtain an analytical solution of the Navier-Stokes equation. The resulting working equation of the instrument is constrained to small amplitudes of vibration. Deviations from the theoretical behaviour of the instrument were explained by different effects like interactions with the electric measurement circuit (Padua, 1994) or non-linear characteristics of the oscillator (Aumann et al. 2000). The dependence of the viscosity on the wire's amplitude squared, observed by Wilhelm (1998), could not be explained. For slightly larger amplitudes, the Boundary Layer Theory indicates axis symmetry of the flow field which is supported by flow visualisations published by van Dyke (1982) as well as CFD simulations performed in this work. Solving the Navier-Stokes equation applying axis symmetry, a group of inertia terms remains in the equation otherwise cancelled in Retsina’s solution for small amplitudes. These findings agree with the dependence of the results on the amplitude squared. In CFD simulations of the flow field, the fluid-structure interaction allows to compare the working equation of the instrument with the complete Navier-Stokes equation by means of the force exerted on the wire. Fluid properties, amplitude and frequency of the wire were varied over wide ranges in the CFD simulations. Deviations between the working equation and the CFD results define the range of $Re$ numbers and amplitudes for the working equation to remain valid. Additionally, the transition at initiating the wire motion is investigated as well as the point of flow separation at the vibrating wire. This defines the operating range of the instrument.
The Effect of Multi-Walled Carbon Nanotubes on Thermal Behavior of 1-Butyl-3-Methylimidazolium Hexafluorophosphate

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The composites of ionic liquids (ILs) and carbon nanomaterials possess a number of features, which make them attractive for various technical applications. The information about interaction of IL ions with solid surfaces is rather contradictory and needs additional investigation. In this work, we report the results of calorimetric study of 1-butyl-3-methylimidazolium hexafluorophosphate \([\text{C}_4\text{mim}]\text{PF}_6\) and its composites containing high mass fraction of stacked-cup multi-walled carbon nanotubes (CNT). Heat capacity of three polymorphs of \([\text{C}_4\text{mim}]\text{PF}_6\) was measured in the temperature range 5 K – \(T_{\text{fus}}\), and heat capacity of the liquid phase was measured to 370 K. Parameters of the solid-phase transitions and fusion for various polymorphs were determined. The temperature ranges of stability for various phases were delimited. If a composite contained \(w(\text{CNT}) \leq 20\%\), no statistically significant changes in heat capacity and temperatures of phase transitions of \([\text{C}_4\text{mim}]\text{PF}_6\) compared to pure IL was observed. The results were independent on the fact whether CNT remained hollow or were filled with the liquid. However, at \(w(\text{CNT}) \geq 80\%\) we observed the changes in thermal behavior of the composites. The contribution to heat capacity from IL interacting with CNT was identified. This contribution demonstrated gradual increase starting at 190 K, and the resulting heat capacity at high temperatures exceeded that of bulk \([\text{C}_4\text{mim}]\text{PF}_6\).

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The flow properties of blood are an important factor in the evaluation of blood disease on the medicine, but the method of viscometry and the data collection are not so easy. In particular, Human arterial blood is so difficult practically. This study has been described on the viscosity measurement and their evaluations for horse arterial blood. A compact-sized falling needle rheometer with quick operation and automatic flow analysis has been developed for viscometry of blood, and the relationship between the apparent viscosity and physical properties of blood have also been evaluated. Measured flow properties of blood are evaluated as a flow curve showing the relationship between the shear stress and shear rate. Observed flow curves of bloods show three typical fluid regions, these are, the Non-Newtonian fluid region for a low shear rate range, the transition region and the Newtonian fluid region for a high shear rate range. Flow properties of blood in the Casson fluid region and the apparent viscosity in the Newtonian fluid region are measured, and they are compared between horses. A non-linear relationship between the hematocrit value, that is, the volume percentage of red corpuscles in the horse arterial blood, and the apparent viscosity are observed. Finally, Flow properties of other mammalian bloods including horse blood are discussed on the effect of hematocrit values to blood viscosities.
Cage Occupancy of Hydrogen Molecules in the Structure I, II, H, and VI Hydrates

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Hydrogen is an interesting target as a guest molecule of clathrate hydrates, because hydrogen molecule is enclathrated in the hydrate cages and simultaneously migrates relatively-freely through hydrate cages. In this presentation, the cage occupancy of hydrogen molecules in the structure I, II, H, and VI hydrates will be summarized.
An Ultrafast Multiple-Wire Microchip to Measure the Thermal Conductivity and Thermal Diffusivity of Gases

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Based on a silicon microchip, a miniaturized thermal transport-properties sensor was constructed. It allows the measurement of thermal conductivity and thermal diffusivity of less than 1 ml gas within a few milliseconds at a very low heating power. The microchip contains a 2000-µm-wide 300-µm-deep channel that is spanned by a series of thirteen unsupported bridges. These serve as one hot and twelve cold wires, acting respectively, as the heat source and the thermometers of the sensor. The cold wires are arranged symmetrically to the center hot wire at six different distances between ±50 µm and ±500 µm. To ensure high signal resolution, each thermometer is switched to its own Wheatstone-bridge circuit of the external IO-unit. The thermal conductivity is determined using the quasi-steady-state (QSS-) technique [1]. Here, a step pulse of a few milliseconds is applied to the hot wire while measuring the quasi-stationary response of selected pairs of thermometers. Their individual differences in temperature furnish the measurand on a redundant basis. The thermal diffusivity results from a time-of-flight measurement: a 100-µs-pulse is fed to the hot wire from where the resulting heat pulse propagates through the gas, in both ways passing one cold wire after the other. For each one of them, the arrival of the temperature maximum is detected. Again on a redundant basis, the thermal diffusivity is evaluated from all these points in time. A preliminary assessment reveals standard uncertainties for both measurands mentioned to be well below 5 %.

References

Study of temperature pressure dependences of mixtures consisting of hydrocarbons and water important for practical us, as natural hydrocarbons mixtures as a rule are in contact with water. The results of such examination are important and for the theory, as give information on interaction between polar and nonpolar molecules. Temperature dependence of pressure is determined on isochores, including temperatures of phase transition a liquid-liquid and liquid-vapour. Original construction of high-temperature adiabatic calorimeter allows to us him also as a piezometer of constant volume and to measure in the same experiment isochoric heat capacity and PVT-properties n-heptane containing 0.147 mole fractions of water mixture in large region of temperatures. The temperature dependence of pressure is determined on isochors, including a liquid-liquid and liquid-vapour phase transitions.

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Argon Fundamental Asymmetric Equation of State

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In this paper the method of construction of the equation of state (EOS) which satisfies the requirements of the virial EOS and scaling EOS which account for the asymmetry relative to the critical isochore. The method is based on the Benedek hypothesis [1] and the phenomenological theory of critical phenomena [2, 3]. Standard deviation calculated by the EOS of this work and the experimental data was in a single-phase region: density 0.21%; pressure 0.39%; isochoric heat capacity including a wide neighborhood of the critical point 2.7; speed of sound 1.7%; isobaric heat capacity 0.9%. The proposed method is tested on the example of the construction of the argon asymmetric EOS. Calculated tables of equilibrium properties of argon in a wide range of state parameters: density from 0 to 3.35 critical density, temperature from the triple point to 1200 K. Also calculated detailed thermodynamic tables for critical and metastable parts of thermodynamic surface. It is shown that the accuracy of the description of the isochoric heat capacity in the critical region of suggested equation of state is significantly higher than crossover equation [4] and accuracy description of the density and sound speed in the metastable region corresponds to the experimental. Standard deviation calculated by the EOS of this work and the experimental data in the metastable region was: density 0.08%; speed of sound 1.2%.

References

While it has been observed that porous materials can undergo structural changes upon fluid adsorption, molecular simulations of fluid adsorption often revert to the use rigid frameworks. One of the main reasons for employing this simplifying assumption has to do with the adsorbent forcefield (i.e., interaction parameters for the solid) and its ability to faithfully reproduce the phase behavior of the bare adsorbent, which is often overlooked. Another important reason is that structural changes upon fluid adsorption involve concerted motion of many atoms/molecules, which can be difficult to capture reliably using brute force simulation methods. In this work, we present a relatively simple approach to study fundamental aspects of adsorption in flexible materials using molecular simulation [1]. The approach employs flat-histogram sampling, which has been shown to be an efficient method to calculate adsorptive properties in rigid frameworks [2], and takes as input information about the inherent thermodynamic stability of the adsorbent material. We are able to reproduce well-known, yet non-trivial, "breathing" behavior and uncover its underlying physics. In addition, we will present results exploring the interplay between capillary phase transitions and structural phase transitions.

References

Hydrate Model for CCS Relevant Gases Compatible with Highly Accurate Equations of State – I. Parameter Study and Model Fitting

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In this study, a gas hydrate model for pure CO₂ hydrates [1] was extended to eight hydrate formers, which are especially relevant in CCS applications. The hydrate model was adopted from the model of Ballard and Sloan [2], which is based on the van der Waals and Platteeuw [3] theory (vdWP). The new model is compatible with highly accurate equations of state (EoS) for other phases than hydrate given in the form of the Helmholtz energy or the Gibbs energy. A detailed analysis of the main parameters of the vdWP-based model including the specific hydrate volume, the Langmuir constant, and the EoSs employed for other phases was carried out. A new correlation based on the Murnaghan equation of state for solids [4] was developed for the volume of gas hydrates. The correlation provides reasonable prediction for the lattice parameter over wide pressure and temperature ranges for a large variety of si and sII hydrates. This represents an important improvement compared to other correlations considered in some previous vdWP-based hydrate models. A comprehensive procedure for fitting the hydrate-model parameters (the reference properties, and the Kihara potential parameters) with the Levenberg-Marquardt algorithm was developed. The chemical potential of water for three-phase equilibria with hydrates and various hydrate composition data (hydration number and cage occupancies) can be used in a multi-property fit to determine the model parameters. The uncertainties of the experimental data were thoroughly studied in order to define a dimensionless quality criterion for the multi-property fit.

References

The polar and perturbed form of the statistical associating fluid theory (Polar PC-SAFT) was used to model lower 1-alcohol-alkane system. The ability of the equation of state to predict accurate activity coefficients at infinite dilution for 1-alcohol in alkane was demonstrated. Moreover, extents of association are compared to experimental data and MD simulations demonstrating the impact of considering polar interactions. Pure component parameters fitted for alcohols were then extrapolated to approximate pure water SAFT parameters which were validated through predicting the extent of association for the pure component, the solubility and the activity coefficient at infinite dilution for water in alkanes. Results show good agreement with experimental data and MD simulation demonstrating the theory’s predictive power as well as the importance of considering polar interactions for better hydrogen bonding thermodynamics.
Aqueous hydrocarbon systems are of considerable interest in many applications ranging from the petrochemical industry to biological process and environmental protection. A comprehensive understanding of the phase and interfacial behavior for such systems is important to improve these applications. In the presentation, we first discuss the development of Monte Carlo simulation methods for determining the bulk and interfacial properties of systems that exhibit liquid-liquid phase separation. We present a series of results for a binary Lennard-Jones system that exhibits complex bulk phase behavior. We next show how these approaches are applied to realistic models of water-octane systems in the vicinity of mineral surfaces. For the bulk system, we trace water-rich liquid-vapor (VLE), octane-rich liquid-vapor (VLE), and liquid-liquid (LLE) saturation curves over a wide range of temperatures, pressures and compositions. These curves are constructed via a combination of direct grand canonical simulations and various expanded ensemble schemes. Analogous techniques are used to calculate interfacial properties of the water-octane mixture at a silica surface. We present results that show how wetting properties, such as the contact angle of a water droplet at a silica surface in a mother octane phase, evolve with temperature, pressure, and composition.
Spatially Resolved Acoustic Spectroscopy (SRAS): from Surface Acoustic Waves Velocities to Crystallographic Orientation

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The microstructure and properties of a material determine its characteristics such as strength and stiffness. The laser ultrasonic technique spatially resolved acoustic spectroscopy (SRAS), which generates surface acoustic waves (SAW) thermoelastically, is a robust and rapid method to quantitatively measure the velocity of SAW propagating on the material's surface. The topographic map of velocity is obtained and shows the contrast of grains. We developed a forward model which predicts the SAW velocity for all the combinations of plane and SAW propagation direction of a material based on its elastic constants. The purpose of the work presented is to determine the orientation of the crystal or grain according to the measured SAW velocities in a limited number of directions. A search algorithm, termed the overlap function, solves this inverse problem and is tuned for SRAS results which present data as a velocity surface spectrum. The orientation results of a range of industrial materials, such as nickel-based alloys, titanium-based alloys and stainless steels, have been presented with comparison with electron back-scattered diffraction technique. We discuss the influence of number of directions in the SAW velocity measurements which affect the accurate determination of the planes. The implementation of this technique utilizes the triangular relation of three elements – elastic constants, crystallographic orientation and SAW velocities – by knowing any of the two, the third one can be achieved. However, it is possible to determine the elastic constants by SAW velocities on multigrain materials without knowing the orientation of grains. The feasibility study of cubic structure materials are demonstrated.
Measurements of thermophysical properties of liquid metals are demanding and thus rare. A recently published data collection provides high temperature data for a set of 22 metals [1]. Although the measurements concern data in the range up to 5000 K, the critical region however, is mostly far beyond the region accessible experimentally at present, with exceptions of Alkali metals. Knowledge of the phase diagrams and of the critical data is important for high-temperature technologies and also of fundamental interest. Therefore an attempt is made to extrapolate the available data into the critical region. A novel approach for extrapolating the density data [2] is applied taking into account recent theoretical developments in the field of critical phenomena, which are the crossover from the universal criticality of the 3d-Ising model towards mean-field behavior, and the theory of complete scaling that describes the nonlinearity of the diameter of the phase diagrams. The method is tested on phase diagrams of Cesium, Rubidium, and Mercury for which accurate phase diagrams up to the critical region are available and compared with simulation results and other estimation methods e.g. such that are based on inter-atomic potentials or surface tension measurements. Comparison is made with measurements of the critical temperature by the 'exploding-wire technique’ e.g. of Gold, Lead and Zinc. Corresponding state behavior of the metals is established.

References

Relative acoustic gas thermometry leads us a better understanding of the difference between the thermodynamic temperature (T) and the International Temperature Scale of 1990 (T90). By measuring the ratio of the speed of sound along the reference temperature isotherm and the unknown temperature isotherm, the thermodynamic temperature can be determined with an uncertainty several times lower than present temperature scale. There are limited thermodynamic temperature measurements at temperature higher than 500 K. The measurements of a prototype cylindrical microwave cavity using Nickel-Chromium alloy confirmed the possibility of developing high temperature acoustic thermometry up to the copper point. NIM (National Institute of Metrology, China) is now in the progress of investigating primary acoustic gas thermometry at temperature higher than 800 K with the collaboration with NIST. The cylindrical acoustic and microwave resonator was used because of the stable mechanic structure and the convenience of machining and assembling. The room temperature acoustic transducers with high temperature alloy acoustic ducts were used to measure the acoustic resonant frequencies in argon. The thermal expansion of the cavity was measured by the homemade microwave transducers. The signal to noise ratios and quality factors of acoustic and microwave responses were measured at different temperatures. The ratios of the acoustic and microwave resonant frequencies between high temperature and room temperature were compared between different modes. Those acoustic and microwave techniques can also be used to measure the speed of sound and refractive index of working fluids at temperature high up to 1360 K.
The Mechanism of Cinobufotalin Probed by Fluorescence Spectroscopy

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Cinobufotalin has double effect of inhibiting tumor growth and stimulating the immune system, and is widely used in cancer clinic. The mechanism of action of which remains unknown. Human Serum Albumin (HSA) is the most abundant carrier protein in blood circulation. The interaction between cinobufotalin injection and HSA in physiological buffer (pH 7.4) was investigated by fluorescence spectroscopy. The fluorescence spectrum of the interaction between different doses of cinobufotalin and HSA showed that the fluorescence intensity of the reaction solution firstly increased and then decreased with the increase of dose of cinobufotalin injection, which was caused by fluorescence intensity stack and fluorescence quenching. The results of fluorescence spectrum at three temperature (300K, 310K, 315K) showed the degree of binding at 315K is higher than that at 310K and 300K. The results indicate that it is obvious that the effect of the different doses of cinobufotalin on the interaction, and the combination is better under proper high temperature than under low temperature. In addition, from the analysis of the experiment data, the fluorescence quenching mechanism for HSA through cinobufotalin injection binding is coexistence of static and dynamic quenching, but the dynamic quenching is dominant.
Cinobufotalin has double effect of inhibiting tumor growth and stimulating the immune system, and is widely used in cancer clinic. The mechanism of action of which remains unknown. Human Serum Albumin (HSA) is the most abundant carrier protein in blood circulation. The interaction between cinobufotalin injection and HSA in physiological buffer (pH 7.4) was investigated by fluorescence spectroscopy. The fluorescence spectrum of the interaction between different doses of cinobufotalin and HSA showed that the fluorescence intensity of the reaction solution firstly increased and then decreased with the increase of dose of cinobufotalin injection, which was caused by fluorescence intensity stack and fluorescence quenching. The results of fluorescence spectrum at three temperature (300K, 310K, 315K) showed the degree of binding at 315K is higher than that at 310K and 300K. The results indicate that it is obvious that the effect of the different doses of cinobufotalin on the interaction, and the combination is better under proper high temperature than under low temperature. In addition, from the analysis of the experiment data, the fluorescence quenching mechanism for HSA through cinobufotalin injection binding is coexistence of static and dynamic quenching, but the dynamic quenching is dominant.
Measurements of volumetric properties of binary mixture 0.95 CO$_2$ + 0.05 CH$_4$ were performed at 300.15 – 313.15 K and 8.0 – 10.0 MPa, which is at the vicinity of the critical point in the supercritical state, with intervals 1.0 K and 0.2 MPa for temperature and pressure, respectively, by single sinker densimeter. The extended uncertainties ($k=2$) of measurement are estimated to be 21.5 mK for temperature, 3.39 kPa for pressure, and 0.024% for density. The combine density uncertainty is 0.042% - 0.048% at the measuring range. The uncertainty contribution from molar fraction to density is possibly up to 0.115%, with mixture preparation and gas absorption and desorption effect as the domination factors. The measurement results were compared with GERG-2004 equation of state. Generally, the deviation from experiment data to GERG-2004 EOS increases when approaching to the critical point, peaking at -4.8% at (301.07K, 7.97 MPa). In an isothermal state with increasing pressure, the deviation reaches maximum when crossing the Widom Line. The isobaric expansibility $\alpha_p$, i.e. $(\partial V/\partial T)_p$, was calculated from the experiment results and a maximal locus of $\alpha_p$ in the measuring range is obviously observed. The maximal locus stretches close to critical point but the critical point is not on the extension of this maximal locus. This phenomenon is different with that in purity, for which critical point is on the extension of the maximal locus of $\alpha_p$. 
We have confirmed 8 factors on thermal conductivities of polymer composites to obtain our conductive model, and especially found that the effect of thermal contact resistance of fillers was important, then obtained highly thermal conductive composite. We will show those factors and preparation and evaluation of the highly conductive composite (carbon material/PPS and BN/liquid crystalline polymer composite etc.).
One of the most important subjects in thermodynamic property research field is to determine the universal gas constant, R, or the Boltzmann constant, k, to contribute to the re-definition of the thermodynamic temperature. The most promising experimental approach is speed-of-sound measurement for gas, so called acoustic gas thermometry (AGT). Recent progress in AGT techniques remarks the relative uncertainty for the universal gas constant being less than 1 ppm. On the other hand, other experimental techniques such as dielectric constant gas thermometry (DCGT), Johnson noise thermometry (JNT), or Doppler broadening thermometry (DBT) are competitive for the moment. In this study, therefore, a completely different approach to determine the universal gas constant was proposed. Namely, the universal gas constant is determined from gas-phase PVT property measurements. Since density calibration techniques for solid sample are well established recently, it is possible to improve measurement performance in gas density measurements to ppm level. In the present study, apparatus for gas-density measurement using a hydrostatic weighing of 1 kg silicon sphere was designed. By measuring buoyancy force acting on the sphere, gas density can be measured with an uncertainty around 1 ppm. The gas pressure is measured by a dead weight piston-cylinder balance which is calibrated against the national pressure standard in NMIJ. The apparatus is thermostatted at 273.15 K with good temperature stability of less than 0.1 mK. The present status of this study, estimated measurement uncertainties, gas samples considered is presented.
Gas hydrates are ice-like solids, where molecular cages of water surround light hydrocarbon species at high pressure and low temperature. In conventional energy pipelines, exposure to cool seawater temperatures may lead to the rapid growth of hydrate particles and blockage of the pipeline. In the past decade, a new hydrate management strategy has emerged, where the injection of anti-agglomerant (AA) chemicals can prevent the formation of large hydrate aggregates or wall deposits. In limited case studies, AAs have been successfully deployed to generate a flowable hydrate-in-oil slurry without the formation of a blockage. In this paper, we present a comprehensive review of hydrate-wall adhesion forces, based on over ten years of experimental research using a micromechanical force (MMF) apparatus. The basic physics of hydrate adhesion is based on a capillary liquid bridge between the hydrate particle surface and pipeline wall. By injecting both ionic and nonionic surfactants, the interfacial tension of the bridge may be sufficiently weakened as to eliminate the functional deposition force. More recent investigations have focused on physical alteration to the pipeline surface roughness, which has been shown to control adhesion force. Together, the data support the use of a revised physical model to predict hydrate adhesive force in a four-phase adhesive system; we present a theoretical model for this force based on the free energy of the capillary bridge.
Ab Initio Molecular Dynamics Study of Methane Hydrate Thermophysical Properties

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Ab Initio Molecular Dynamics (AIMD) simulations are performed for fully occupied methane hydrates. Methane hydrates are crystalline compounds which consist of cages of hydrogen-bonded water molecules that entrap methane at high pressures and/or low temperatures. They exist naturally near continental margins and in permafrosts and are believed to contain an energy content that is twice that of all other fossil fuels combined. Their thermophysical properties have been primarily determined experimentally although there is a lot of disparity among the results of different research groups. Nevertheless, these properties are essential for producing natural hydrates and performing risk assessment studies for the production process, so an ab initio method was used in this work in an attempt to provide more accurate results. The temperature range considered is 210K-323K which is suitable for energy-storing hydrates in natural settings. The second-order elastic constants, thermal expansion coefficient, and heat capacity are evaluated as functions of temperature. The elastic constants are used to follow the stability of the hydrate lattice at different temperatures, and the results are compared with experimental values. These results constitute the first ab initio set for methane hydrates and complement our previous work that established the elastic isotropy of these compounds and their ideal strength in different directions using Density Functional Theory.
Effect of Thermodynamic Inhibitors on the Nucleation Driving Force of Gas Hydrates

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Although it is well known that thermodynamic gas hydrate inhibitors modify the incipient formation point of gas hydrates, only few efforts have been performed to establish how this chemical compounds modify the formation kinetics of gas hydrates. For instance, Yousif et al. (1996) determined experimentally that, a small amount of methanol increases the rate and amount of forming hydrates, acting as a gas hydrates promoter!!. Taking into account that the driving force of nucleation is crucial for establishing whether a phase may or not form, in this work, the effect of the most common thermodynamic inhibitors on the driving force of multicomponent gas hydrates is assessed from a theoretical point of view. The corresponding results obtained from three mathematical expressions are compared: the Christiansen-Sloan, the Kashchiev-Firoozabadi, and one suggested by Carreón-Calderón et al. The results show that the nucleation driving force obtained using the different expressions are in agreement with experimental observations; that is, driving force increases in the presence of small amounts of thermodynamic inhibitors, facilitating the formation and stability of gas hydrates.

References

Cohesive Force Measurement Between Precipitated Asphaltene Solids

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Asphaltenes are the heaviest and most polar components of crude oils and may precipitate in reservoirs, wellbores and flowlines, due to the rapid decrease in fluid pressure during flow or through co-mingling of hydrocarbon streams. While the consequence of asphaltene deposition and build-up at the wall is well characterised, little is known about how precipitated asphaltene particles behave in flow. In this presentation, we discuss adaptations to a micromechanical force (MMF) apparatus that enable measurement of cohesive force between asphaltene particles. The results demonstrate that asphaltene cohesive forces may be up to twice those measured previously for the well-studied gas hydrate system, with solid-solid cohesion as the primary mechanism. MMF data provides further insight into the asphaltene particle surface free energy. The cohesive force data demonstrate that this free energy is very sensitive to the type of crude oil from which the asphaltenes were extracted, suggesting the potential for MMF-based studies to characterise the inherent activity of the asphaltene species within crude oil. In addition, co-precipitated resinous material on the surface of the asphaltene particles has been demonstrated to cause a uniform shift toward higher cohesive force, suggesting that these active resins may function to modify asphaltene surface free energy. The dependency of the inter-particle forces on the type of asphaltene (particle agglomeration size, agglomeration time, source crude oil, precipitation technique) will also be discussed.
Conversion of in situ methane hydrate over to carbon dioxide dominated hydrate through injection of carbon dioxide has proven feasible even up to pilot scale in Alaska. The use of carbon dioxide mixed with nitrogen increases permeability and reduces risk for blocking pores with new hydrate. As a consequence of the first and second laws of thermodynamics the most stable hydrate will form first in a dynamic situation, which involves that carbon dioxide will dominate the first hydrates formed from water and carbon dioxide / nitrogen mixtures. This selective formation process is further enhanced by favorable selective adsorption of carbon dioxide onto mineral surfaces as well as onto liquid water surfaces, which facilitates efficient heterogeneous hydrate nucleation. Given this favoritism of carbon dioxide in the new hydrate formation the question is whether the carbon dioxide will be stored safely or affected in thermodynamic stability by a contacting gas phase with reduced content of carbon dioxide. In this work we apply residual thermodynamics (ideal gas phase as reference) for all components in all phases as basis for a free energy analysis of hydrate stability. It is found that if the flux of gas through the reservoir is high enough to prevent the gas from being depleted for carbon dioxide prior to subsequent supply of new gas, then combined carbon dioxide storage and natural gas production is still feasible. Otherwise gas dominated by nitrogen will still dissociate the methane hydrate if the released in situ methane from hydrate do not mix in with the nitrogen dominated gas. The ratio of nitrogen to carbon dioxide in such mixtures is therefore a sensitive balance between flow rates and rates for formation of new carbon dioxide dominated hydrate.
Heat Capacities and Acoustic Virial Coefficients for a Synthetic Coal Mine Methane Mixture by Speed of Sound Measurements

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Coal mine methane (CMM) and other kind of coal seam gases are by products obtained from coal mining. These gases are a safe issue inside mines because they might be explosive if they are mixed with air in certain proportion. Nowadays, they are more often used as energy source, but in order to improve the performance and achieve higher efficiencies, accurate thermodynamic properties and equations of state are required. Unfortunately there is a lack of these gas mixture properties. Some equations of state as GERG-2008 were developed to predict natural gas like mixtures. However, coal mine methane composition is significant different and, therefore, experimental measurements are necessary to compare reliability of the equation of state and theoretical properties. This study is focused on obtaining accurately some thermodynamic properties such as isobaric and isochoric heat capacities, adiabatic coefficient as perfect gas and acoustic virial coefficients of a synthetic coal mine methane mixture at two different temperatures (250 K and 273.16 K). These properties are calculated using acoustic resonance to measure speed of sound and extrapolating to zero pressure. A spherical resonator was used for the measurements of the speed of sound for the CMM mixture. It is equipped with two capsule-type platinum resistance thermometers which provide a standard uncertainty in temperature measurements of ± 1 mK at 273.16 K. The pressure is measured by means of two resonant quartz-crystal manometers for the pressure ranges (0 to 2) MPa and (1 to 20) MPa with a relative standard uncertainty of ± 1·10^{-4} Pa/Pa. The total uncertainty of the speed of sound is not worse than 0.02%. The results have been compared with the GERG-2008 equation of state.

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Li-ion secondary batteries (LIBs) are considered to be the most promising candidate for personal automotive vehicles, when considering their rather low weight. Large format LIBs require a good understanding of the thermal behavior, especially during charging at high rates. In addition, to avoid the thermal runaway is the main safety issue when a battery is in use. Therefore thermal management and knowledge of the internal heat distribution is crucial. This requires the determination of heat sources as well as the thermal conductivity of all different battery components. Burheim et. al [1] recently reported thermal conductivities of some electrode materials and discussed different heat sources inside a LIB. The thermal conductivity of a separator has not been reported so far. The aim of this work is to be able to model internal heat distribution inside LIBs for some combinations of commercial available electrode materials and separators. The apparatus is described in great detail in [2]. It is able to measure the heat fluxes as well as the sample thickness and the temperature drop over the sample. The measurements were carried out with and without electrolyte (50:50 vol% EC/DEC), at different compaction pressures of 2.3 bar up to 11.5 bar. It is shown that the presence of an electrolyte as well as the compaction pressure have a significant influence. The presented 2D thermal model of a LIB is constructed using non-equilibrium thermodynamics. We give the internal heat distribution for various combinations of materials at different operating conditions.

Acknowledgments

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References

Improving Thermodynamic Consistency Among Vapor Pressure, Heat of Vaporization, and Liquid and Ideal Gas Isobaric Heat Capacities through Multi-Property Optimization

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Vapor pressure, heat of vaporization, liquid isobaric heat capacity, and ideal gas isobaric heat capacity can be measured for pure organic compounds between the triple point and critical point. Additionally, heat of vaporization is proportional to the derivative of vapor pressure with respect to temperature through the Clapeyron equation, and the difference of liquid and ideal gas heat capacities are proportional to the derivative of heat of vaporization with respect to temperature. These relationships and experimental data were compared for several compounds to interpolate and extrapolate available data and increase consistency amongst these properties. A methodology for assessing the thermodynamic consistency amongst data sets and optimizing the accepted property values has been developed so that this procedure can be applied to other compounds in the DIPPR 801 database for which there are fewer experimental data available. The process involves critically evaluating available experimental data and the correlations used to fit these temperature-dependent properties. Multi-property optimization includes weighting the various data values based on the accuracy of the data and on the perceived relative importance of the properties in process design. User-defined weighting systems will be established to provide optimization flexibility across these properties for future use of the DIPPR 801 database.
We report on our recently accomplished measurements of the surface tension of supercooled water (J. Phys. Chem. Lett. 5, 2014, 425–428), and the first series of measurements for the density of supercooled water at elevated pressures. The goal of both studies is achieving reference-quality data in the region of supercooled water extending close to the ice homogeneous nucleation limit. This activity is primarily motivated both by the fundamental interest in the properties of supercooled water and by its importance in nature and technology, particularly in atmospheric sciences and aerospace engineering. The research is also inspired by needs of the International Association for the Properties of Water and Steam (IAPWS) which works on extending the accurate analytical formulations of thermophysical properties of water down to the region of supercooled water.

The surface tension was measured down to $-25^\circ$C using a modified capillary rise method. Only a short part of the fused silica capillary was maintained at the temperature of interest, while its rest and the water pool were kept at the ambient temperature. The most interesting result was that the data points represent an almost straight-line extrapolation of the dependence of the surface tension on temperature found in the stable region (positive Celsius temperatures). This is in contrast with the older data by Hacker (NACA TN 2510, 1951) showing an anomalous temperature course characterized by a second inflection point. This claimed anomaly received a partial support by some molecular simulation studies and theoretical models, but most likely it was an experimental artifact. In addition to our published work, we discuss most recent experiments using alternative experimental methods and attempts to extend the temperature range.

The goal of the measurements of the density of supercooled water is achieving highly accurate data (0.02% in density or better) for supercooled water in a region limited by the ice homogeneous nucleation temperature at the given pressure and up to 200 MPa. The data should provide a basis for the development of an accurate equation of state (EoS) for cold and supercooled water. The existing data sets either do not cover a sufficient range of temperatures (Sotani et al., High Temp. High Pressures 32, 2000, 433), or show too high uncertainties (Mishima, J. Chem. Phys. 133, 2010, 144503) making them unsuitable for the development of an accurate EoS. Our density measurements are a work in progress. We present the experimental method and preliminary data not yet covering the full pressure and temperature ranges.
The Measurement of Argon Viscosities by the Two-Capillary Viscometry from 200 K to 650 K

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Argon is the monoatomic gas that plays an important role in the primary acoustic thermometry because of its proper properties and specific isotopes. The viscosity of argon at variant temperature is the key parameter for the state-of-the-art primary acoustic thermometers. The accurate viscosity values of argon are especially important for primary acoustic thermometers working at high temperatures. The uncertainty less than 0.1 % for the viscosity values is requested. Currently, the two-capillary thermometry demonstrates the relative standard uncertainty less than 0.04 % of the measurements of argon viscosities from 200 K to 400 K. The measurements by the oscillating – disk viscometers have yielded the data at temperatures from 290 K to 680 K with the uncertainty from 0.1 % to 0.2 %. On the other hand, the ab initio calculations have yielded the data of argon viscosity in the wide temperature span from 1 K to 10000 K. The comparison has demonstrated the good agreement of the relative differences within 0.1 % among those experimental and the ab initio calculations in the overlapping temperature ranges. In this report, we present the new measurements of argon viscosities at temperatures from 200 K to 653 K by the authors upon the two-capillary viscometry. The relative standard uncertainty of the measurements is estimated to be 0.062 %. Besides the measurement results, we will discuss the observations with the two-capillary viscometer and the uncertainty sources with the measurements.
Densities and Viscosities of (1-Butanol or 2-Butanol + 2,2,4-Trimethylbenzene) Mixtures at High Pressures

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There are many mixtures of interest for the development of next-generation biofuels due to the wide variety of oxygenated additives of renewable origin that can be used but there is a lack of information about their properties. This study focuses on the thermophysical characterization of new blends of 1-butanol or 2-butanol, as oxygenated compounds of renewable origin, and 1,2,4-trimethylbenzene, as aromatic hydrocarbon, through density and viscosity measurements, to contribute to the international effort towards development and use of environmentally sustainable fuels. Densities were measured by means of an automated Anton Paar DMA HPM vibrating-tube densimeter which was automated and has an estimated uncertainty of ± \(7 \times 10^{-4}\) g cm\(^{-3}\) (k=2) at temperatures below 373.15 K. A vibrating-wire viscometer has been developed for the accurate measurement of viscosities for pure compounds and mixtures over the working range T = (293.15 to 373.15) K and p = (0 to 140) MPa. Rigorous uncertainty calculations gave a standard uncertainty of the dynamic viscosity of ± 0.5%. Densities and viscosities of binary mixtures (1-butanol + 2,2,4-trimethylbenzene) and (2-butanol + 2,2,4-trimethylbenzene) are reported at four temperatures (293.15 K, 313.15 K; 333.15 K and 353.15K) and pressures up to 140 MPa, as first characterization of biofuels. The experimental data are compared with well-known correlations.

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In this work, CO2 and CH4 type sI hydrates have been studied using electronic Density Functional Theory (DFT) and the Quantum Theory of Atoms in Molecules (QTAIM). Both types of cells included in the structure of type sI hydrate were modeled as isolated independent rigid cages, either empty or containing any of the two selected guest molecules, with single occupancy. Interaction potentials of guest molecules with the enclathrating cell, and the potential profiles when moving between neighbour cells were calculated using B3LYP/6-311+g(d,p) DFT approximation, considering the cases with and without long range Coulombic corrections. The selected theory level was validated by comparison of the estimated Raman spectra with the experimental ones, for both types of cells. Fermi resonance between vibrational bands of CO2, resulting from anharmonic effects, was described using a perturbation procedure intended to estimate the theoretical non-mixed states. The validity of the theory level selected has been stated, and the high anisotropy of the guest-cell interaction potential for the molecules analysed is shown, which may be considered in the formulation of hydrate thermodynamic models as equations of state, and also for the description of transport properties. In addition, the presented results suggest that the hydrate guest occupancy might be calculated from the comparison of experimental and predicted Raman spectra.
Emissivity Measurement under Vacuum from 1.2 μm to 100 μm at PTB

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The accurate knowledge of the emissivity of a material is crucial for a variety of technological applications whenever heat transfer by radiation becomes significant. Examples of vacuum applications which require very low uncertainties of emissivity knowledge are absorbers for solar thermal electricity generation and coatings of onboard reference blackbodies for benchmark missions in space. The Physikalisch-Technische Bundesanstalt (PTB) operates a facility which allows the accurate measurement of the directional spectral emissivity of samples under vacuum conditions from 1.2 μm to 100 μm in a temperature range from -40 °C to 1000 °C. The emissivity measurement setup is part of the Reduced Background Calibration Facility (RBCF) at PTB where all critical components of the optical path are under vacuum and cooled with liquid nitrogen. Hereby the infrared background radiation is largely reduced and consequently the uncertainty of the emissivity measurement is reduced, too. The scheme for direct emissivity measurements under vacuum is based on the measurement of the spectral radiance of a sample inside a temperature stabilized spherical enclosure with respect to the spectral radiance of two vacuum operated reference blackbodies at different temperatures. Here we present the recent expansion of the spectral working range of our facility to the NIR wavelength range (down to 1.2 μm) and the comparison with the earlier obtained results in the overlapping spectral ranges using different sets of beamsplitters and detectors. We also show that samples with very low emissivity can be measured with sufficiently low uncertainty by taking multiple reflections into account. Finally, emissivity measurements of thin and semitransparent samples, showing interference effects, will be discussed. We observed a phase difference between emissivity and reflectivity measurements of semitransparent samples and propose a mathematical model for its explanation.
Performance Simulation of a Heat Pipe Guarded Hot Plate Apparatus for Thermal Conductivity Measurement

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The ASTM C-177-10 standard establishes the criteria for the laboratory measurement of the steady state heat flux through flat homogeneous specimens when their surfaces are in contact with solid parallel boundaries held at constant temperatures using the guarded hot plate apparatus. In order to make easier the apparatus construction, to improve the accuracy of thermal conductivity measurement and to simplify the analyses for calculating the mean plate surface temperature, a circular line electric resistance has been used at precisely specified locations of the metered section and primary guard plates. The uncertainty of thermal conductivity measurement with a NIST apparatus at 300 K is claimed to be ± 1 %. This paper deals with the substitution of the electric resistances by heat pipes embedded in aluminum plates, for measuring the thermal conductivity of an insulating material, thus making the plate temperature much more uniform. The performance simulation was made with an apparatus that consists of cold, hot and guard plates, together with insulating material and specimen, both with a 0.05 W/m.K thermal conductivity value. Solving numerically the 2D energy equation for the whole system, it can be shown that the temperature uniformity in both hot (at 50 °C) and cold (at 30 °C) plates is better than 0.01 K in the metered section, with the ambient at 25 °C and convection coefficient of 10 W/m².K. The maximum temperature difference along a plane parallel to the hot and cold plates in the metered section of the specimen is less than 0.17 K, less than 2 % of the imposed temperature difference (0.4 K), as required by the standard for lateral uniformity. The simulation also shows that because of lateral heat losses, heat supplied to the hot plate must be slightly more (2.5 %) than the ideal configuration (1 D flow), approximately independent of the imposed temperature difference between hot and cold plates, which makes the correction easier.
Analysis by Resonants Peaks of the Resonant Cavity Signal to Determine the Thermal Properties of Gases at Low Pressure

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In order to developing high efficiency thermal solar collector tubes, it is frequently to use vacuum insulation and therefore it is important to develop simple methodologies to study the behavior of the thermal properties of gases as a function of pressure. In this study, heat transfer in air, at different values of pressure, is studied using the Thermal Wave Resonant Cavity technique. The experimental configuration used, consisted of two parallel plates, one of them is heated by a modulated laser at a given frequency and the other is a pyroelectric sensor, which are separated by an air layer [1]. To regulate the pressure levels in the system, the cavity is connected to a vacuum pump. For each pressure value the photothermal phase and amplitude signals to a fixed cavity size were measured, varying the modulation frequency of the heater [2]. From the analysis of the resonance peaks of the real and imaginary parts of the photothermal signal, the values of thermal diffusivity of air are found [3]. Based on this approach, the value of the pressure, at which it is possible to determine the thermal transport properties of air, is established. The feasibility of using this technique for in-situ measurements for monitoring the quality of the vacuum in thermal solar evacuated tubes is discussed.

References

Nucleation Study for Methane Hydrate by Molecular Dynamics

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Clathrate hydrate are solid crystalline compounds most commonly formed from solution to nucleate a mixed solid composed of water and gas. Understanding the mechanism of clathrate hydrate nucleation is crucial for a fundamental study of formation of these complex structures and their applications. Molecular Dynamics (MD) simulation is an ideal method to observe nucleation at the molecular level because the size of the critical nucleus and the nucleation time are nano scales. Various analysis methods have been developed through MD simulations to analyze nucleation in monatomic systems.[1,2] In particular, the nucleation rate, the critical nucleus size, and the free energy curve can be obtained from mean first-passage time, survival probability, and Yasuoka-Matsumoto methods. However, clathrate hydrate nucleation is difficult to observe in MD simulations due to high free energy barriers, so these methods have not been applied to clathrate hydrate systems. Recently, methane hydrate nucleation has been observed by MD simulations at 255 K and 50 MPa using high performance computing.[3] In this study, we analyzed methane hydrate nucleation using these methods for data generated from MD simulations and verified the applicability of these methods for the methane hydrate nucleation analysis. These methods are also easily applicable to other complex clathrate hydrate structures.

References

The latest fitting techniques used in the development of equations of state for the thermodynamic properties of fluids will be presented. The techniques are applied through nonlinear fitting of experimental data and multiple constraints to control the slope, curvature, and other values of an isoproperty line. Two new parameters have recently become key tools for evaluating equations of state; these are the Gruneisen parameter and the phase identification parameter (PIP). They are more sensitive than other properties, and can highlight areas that need improvement. With a significant number of constraints for the derivatives of these two properties and of heat capacities, speeds of sound, pressures, and so on, an equation of state can be developed that meets the characteristics expected in modern work. The application of these fitting techniques will be demonstrated by the performance of a new equation of state for ammonia.
Version 9.1 of the REFFPROP software will be demonstrated. This version has several new features, including improved convergence of VLE state points, and the ability to plot the full saturation curve, including retrograde states and the critical point, in various diagrams. The REFFPROP program uses the latest high accuracy equations of state based on the Helmholtz energy for the thermodynamic properties with typical uncertainties of 0.1 % in densities, vapor pressures, and speeds of sound, 0.5 % in heat capacities, and 0.1 % in pressure in the critical region. The software allows the user to calculate properties of the liquid, vapor, and supercritical states, including two-phase properties for both pure fluids and mixtures. Over 100 fluids are available in the program, including cryogens, refrigerants, and hydrocarbons. The latest GERG-2008 equation for the properties of natural gas systems is included as a dedicated equation with very high accuracies for typical natural gases found throughout the world. Links with other applications such as Excel, Visual Basic, C++, and so forth are available and example files come with the program.
The molecules in the confined systems play the important role in the lubrication, adhesion and fabrication of nanomaterials. It is important for new physics that relate to finite-size and reduced dimensionality effects. The experimental study of actual molecular films were performed. [1] This study shows that the thermal properties of the molecules in the confined system is significantly different from its properties in the bulk system. The freezing point and melting point depends on the width of the parallel slit pore in those confined system. We study the phase transition of Lennard-Jones particles in the confined system. We performed the Monte Carlo simulation. To realize the sampling in the wide energy space or wide volume space, we employed the multicanonical approach. The conventional Monte Carlo method samples the conformations or coordinates at the constant temperature and the constant pressure. The multibaric-isothermal (MUBA) ensemble and the isobaric-multithermal (MUTH) ensemble was proposed. [2] The MUBA ensemble is aiming for the flat probability distribution in volume space. The MUTH ensemble is aiming for the flat probability distribution in energy space.

References

Magnetorheological (MR) materials have the characteristic that their physical properties can be changed applying an external magnetic field. This is possible because they are formed by a non-magnetizable matrix in which micrometric particles are immersed. The magnetic field induces ordering of the microparticles, generating changes in the physical properties. The most of the studies have been focused on the effects of the magnetic field on the mechanical properties; however the effect of the aligning on the thermal properties as well as the relationship of the thermal transport and viscosity has not been fully understood. In this work, two types of magnetic fluids were studied using carbonyl iron particles in two matrices: silicone oil and silicone rubber. Thermal diffusivity and thermal conductivity of these magnetic fluids are determined using the thermal wave resonant cavity when the fluid is subjected to uniform magnetic fields at different intensities. The dynamic viscosity was also measured and the relationship with the concentration of the particles and the magnetic field strength was investigated. The results show that when the content of carbonyl iron particles is increased in the material, the thermal conductivity and thermal diffusivity are incremented and when the magnetic field intensity increases the thermal conductivity and thermal diffusivity increases even more. A functional dependence of the thermal conductivity and dynamic viscosity was found. Additionally we have shown that using high viscosity materials, the order induced in the microparticles can be kept for a long time and therefore the increase in thermal conductivity can also be maintained.
Statistical Mechanics of Two-Phase, Steady-State Flow in Porous Media

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The study of two-phase flow in porous rocks is relevant to several fluid flow problems encountered in nature; from the study of diffusion of pollutants in water, to enhanced oil recovery from hydrocarbon reservoirs. Regarding two-phase immiscible flow, not much attention has been given to the steady-state case, in which average flow properties, like the velocity of fluids, remain unchanged [1]. The system under consideration is dissipative, with entropy production due to viscous flow, while all liquid-liquid interfaces are assumed to be in equilibrium. Once the oil-water system has reached steady-state, important relations like the fractional-flow vs saturation can be studied. The aim is to predict the effective and relative permeability of the porous material in addition to finding relations between the macroscopic parameters characterizing the flow: saturation, fractional flow rates, pressure gradients and total flow rates. The standard pore-scale numerical modeling of this problem has been to follow the motion of the fluid interfaces by time integration: one solves the Washburn equation, which is a generalisation of the Darcy's equation to take capillary pressures due to the interfaces into account [2]. We report evidence that the whole system, under prevalent flow conditions, (flow rate = 50 mm³/sec, dP/dx = 1000 Pa, dT/dx = 0 K), can be regarded to be in local equilibrium. Monte Carlo simulations have been used to evolve samples or sub-parts of the system till the whole system reaches steady-state, the result being independent of the size of the samples of the system above a certain length scale. We find that the system reaches steady state much faster with the Monte Carlo approach, as compared to its evolution using time integration. Besides speeding up the algorithm to a great degree, the thus established equivalence between time averaging and ensemble averaging, enables us to use statistical mechanics to characterize the flow in terms of local flow parameters, like pressure differences and flow composition.

References

New group-contribution interaction parameters for equation of state based on NIST-modified UNIFAC were reported. The proposed model is combination of Peng-Robinson equation state and Universal Mixing Rule (UMR) proposed by Voutsas and co-workers. Interaction parameters were regressed using critically evaluated vapour-liquid equilibrium (VLE), liquid-liquid equilibrium (LLE) solid-liquid equilibrium (SLE), excess enthalpy (HE), infinite dilution activity coefficient (AINF) and excess heat capacity (CPE) data. This work is a further extension of NIST-modified UNIFAC to high pressure application and consistent with previous publication on low-pressure phase equilibria. The algorithmic framework for quality assessment of phase equilibrium data was applied for qualifying the consistency of data and screening of possible erroneous data. Parameters matrix involves 14 gaseous components and 96 main groups for NIST-modified UNIFAC.
Aquatic Lyrium or Water Hyacinth, alternate names for this plant, is a free floating plant native of the Amazon, Brazil, which by the beauty of its flowers has been propagated to almost all the tropical and sub-tropical regions of the world. This plant is a weed, which causes many consequences extremely unfavorable for the environment and for the diverse human activities that are developed in the bodies of water. Among the most often used methods to control water hyacinth are herbicides, physical removal or drainage, and biological control, none of which has been entirely efficient or profitable. It is for these reasons that arises the need to incorporate other new technologies of control, being in this case the use of ultrasonic irradiations, with certain values of frequency and intensity, in order to induce cavitation in the aqueous structure of Aquatic Lirium, and consequently, inhibit their photosynthetic activity, causing its death. The leaves of aquatic plants are systems particularly useful for studying the effects of bubbles trapped within their structures. For this reason, in this work it was used the photoacoustic technique for monitoring the photosynthetic activity in Aquatic Lirium plant, before and after ultrasonic irradiation. Our results show that the optical absorption bands corresponding to chlorophylls \textit{a} and \textit{b} decrease dramatically in the case of the leaves of the irradiated plants, showing the damage in the chlorophylls and hence the photosynthesis inhibition, which have a remarkable correspondence with the structural damage in the irradiated plants, which is increased with time, in an irreversible way.
Modeling the Thermal Conductivity of Nanofluids Via the Use of Density Scaling

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Casalini and Roland [Phys. Rev. E 69, 062501 (2004); J. Non-Cryst. Solids353, 3936 (2007)] have effectively proved that both the dielectric relaxation times and the viscosity of liquids can be graphically represented into a single master curve as a function of the thermodynamic potential ($T \rho^\gamma$), where $T$ is the temperature, $\rho$ is the molar density, and $\gamma$ is a state-independent scaling exponent. In this work, we applied the aforementioned thermodynamic scaling to the thermal conductivity of novel thermal fluids: namely, nanofluids. The term nanofluid refers to suspensions of nanometric solid particles (CuO, Al₂O₃, etc) in any base fluid (water, ethylene glycol, etc.). Unlike previous studies on density scaling of transport properties, a more suitable normalization of the thermal conductivity of the nanofluid was used in this work in order to obtain improved correlations of thermal conductivity over much wider ranges of temperature and volumetric fraction of the nanoparticle. A calculation procedure is also described here to optimize the value of the scaling exponent $\gamma$ that ensures the best superpositioning of all experimental isotherms considered.
A Cubic Statistical Mechanical Based Equation of State for Metals

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Liquid metals exhibit various invaluable characteristics in industrial applications. High boiling temperatures, extended liquid ranges, high thermal conductivities, low vapor pressures and high heats of vaporization have made them very useful in machine design and processing operations. Therefore a precise knowledge of their thermodynamic properties seems to be extremely helpful. In the case of metals, difficult experimental conditions such as high temperatures and low vapor pressures limit the experimental measurements. This has led many investigators to apply various accurate predictive methods. In this work, an analytical equation of state is proposed for different molten metals in the periodic table. This statistical mechanical based 5th order equation of state is that of Song and Mason in conjunction with the corresponding states correlations of Boushehri and Mason. The purpose of this paper is to present a method for predicting the equation of state of liquid metals from properties that are readily available at ordinary pressures and temperatures. In particular, the latent heat of vaporization and the liquid density at melting point are used as two numbers that can correlate and predict the behavior of liquid metals. These two numbers, if not directly available, can be obtained with sufficient accuracy from two measured vapor pressures and liquid densities. The virial coefficients of metals cannot be expected to obey a law of corresponding states for normal fluids. The unique adjustable parameter of the equation of state, $\gamma$, is used for compensation of any discrepancies in potential function with respect to the Lennard-Jones potential which is used by Boushehri and Mason. The equation of state includes a great range of (main group and transition) metals in a vast range of temperatures from below melting point up to near the critical point and pressures up to 200 MPa with very good accuracies.
Implementation of Isochoric Slopes for Mixture Properties Calculations

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The physical properties of fluid mixtures have been a research focal point for more than a century. Some important reasons were and continue to be the need for efficient and economical industrial processes, engineering design calculations and purely scientific curiosity. Accurate prediction of physical and calorimetric properties of fluid mixtures by an equation of state requires an accurate description of the effects of intermolecular forces between unlike as well as like molecules. The effects of the unlike interactions are especially challenging, because they exist only in mixtures, and they may have strong composition dependence. Experimental measurements for mixtures are required, and the number of measurements required should be minimized. Experimental measurements of derivatives such as $\frac{\partial P}{\partial T}$ have been used previously to evaluate the thermodynamic consistency of equations of state and the impact of using numerical and analytical derivatives during equation development. In this work, we have explored, using different sets of data in a wide pressure and temperature range, the use of isochoric slopes ($\frac{\partial P}{\partial T}$) obtained from $PpT$ measurements to develop correlations that improve the predictions of excess properties. Isochoric slopes are attractive for this application, because they are directly related to energy and entropy calculation, and they depend strongly on composition but weakly on temperature in the single-phase region. The excess properties are calculated using properties for pure substances calculated using reference equations of state and mixture properties that have been measured experimentally. The predicted mixture properties then are compared with experimental data.
Seawater desalination using clathrate hydrate formation is an interesting potential hydrate application, as salt ions are excluded from the clathrate cavities during hydrate formation, thereby resulting in concentrated seawater in the bulk aqueous solution. The resulting hydrate crystals can be subsequently separated from the concentrated seawater and dissociated to produce fresher water. This paper evaluates and reviews, the hydrate based desalination technology which uses low pressure (cyclopentane) and high pressure (methane, methane + ethane) hydrate formers and different hydrate nucleation, growth, and separation methods and the resulting crystal morphology and saltwater removal efficiencies (e.g. [1,2]). A modified van der Waals and Platteeuw (vdWP) model based on statistical thermodynamics has been used to predict hydrate phase equilibria for sII pure cyclopentane (CP) hydrate for different concentrations of aqueous salt solutions. Desalination efficiencies of up to 81 % (salinity decreased from 3.5 wt.% to 0.67 wt.%) can be achieved a bubble column apparatus and different washing/separation methods, including gravitational separation.
Seawater desalination using clathrate hydrate formation is an interesting potential hydrate application, as salt ions are excluded from the clathrate cavities during hydrate formation, thereby resulting in concentrated seawater in the bulk aqueous solution. The resulting hydrate crystals can be subsequently separated from the concentrated seawater and dissociated to produce fresher water. This paper evaluates and reviews, the hydrate based desalination technology which uses low pressure (cyclopentane) and high pressure (methane, methane + ethane) hydrate formers and different hydrate nucleation, growth, and separation methods and the resulting crystal morphology and saltwater removal efficiencies. A modified van der Waals and Platteeuw (vdWP) model based on statistical thermodynamics has been used to predict hydrate phase equilibria for sII pure cyclopentane (CP) hydrate for different concentrations of aqueous salt solutions. Desalination efficiencies of up to 81% (salinity decreased from 3.5 wt.% to 0.67 wt.%) can be achieved a bubble column apparatus and different washing/separation methods, including gravitational separation.
Over the last years, several techniques have been developed to measure the thermal conductivity of thin materials and nanostructures. Among these techniques, the ones that do not require previous preparation and are contactless have been the most attractive. Raman spectroscopy is one of the most powerful spectroscopic methodologies in the study of a great diversity of materials and its multiple uses are still being discovered. Two-Laser Raman Thermometry was developed by J. S. Reparaz et al., and consists of a novel technique to determine the thermal conductivity and thermal field mapping of one- and two-dimensional structures via the changes in their Raman shifts. It consists of inducing a thermal distribution of phonons in a sample using a heating laser and probing the temperature through the spectral position of Raman active mode. In this work the two-laser Raman Thermometry is used to study heat transport in the study of thin materials. Raman scans were performed not only by a line scan but by an area scan in order to have more detail of the thermal field, and the results show the characteristic thermal field previously reported. Thermal conductivity was determined using Fourier’s law and is shown to agree with the values reported in the literature.
High-Resolution Instrument for Measuring the Surface Viscoelasticity of Nano-Bubbles in Water by Ripplon Surface Laser-Light Scattering Method

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The purpose of the present study is to detect Nano-Bubbles (NBs) in water by measuring the differences of surface properties (apparent surface tension and viscosity) between ultrapure water and NBs in water using ripplon surface laser-light scattering (SLLS) method. SLLS method has a potential to detect NBs in the vicinity of the liquid surface by measuring surface properties because this method is capable of observing near liquid surface with the sensitivity of nm order. In order to measure surface properties, we observe surface wave known as ripplon which is excited by thermal fluctuations. The new SLLS instrument we have developed makes it possible to measure surface tension and viscosity with high resolution (less than ±3 % in the case wavelength of observed ripplon is 100 μm). A YAG laser (532nm, laser power 750 mW) is employed and irradiated to the liquid surface as incident light and reference light. We detect both scattering light generated by the incident light and the reference light to take cross correlation. We have observed difference of surface properties between ultrapure water and O2-NBs in water at 25.0 °C. The bubbles were generated for 30 minutes by pressurization and dissolution oxygen. As a result, surface tension of NBs in water decreased about 13 % and viscosity of NBs in water increased about 1.7 times compared to those of ultrapure water after 6 hours from generating NBs. In addition, we have measured temporal change of O2-NBs in water from 40 to 375 minutes after generating NBs. As a result, surface tension decreased and viscosity increased simultaneously. This result suggests that we have observed levitation and stagnation of NBs. We propose the relationship between number density of NBs at the liquid surface and surface viscoelasticity which is related to apparent surface properties.
Isobutane (R600a), isopentane (R601a) and mixtures of isobutane and isopentane are preferred as the working fluid for geothermal organic Rankine cycle systems (ORCs). Accurate thermodynamic properties were the needed for ORC system design and optimization. However, accurate $pvT(x)$ properties for liquid isobutane, isopentane especially for mixtures of isobutane and isopentane are still scare. In this work, an isochoric apparatus is designed and constructed. The density is calculated from the amount of the fluid inside the high pressure cell and its volume. The liquid $pvT(x)$ properties for isobutane, isopentane and mixtures of isobutane and isopentane with R600a mole fractions of 0.2, 0.5 and 0.8 were measured from (260 to 360) K with pressures up to 40 MPa. The uncertainties in the temperature, pressure and density were estimated to be less than 10 mK, 1 kPa and 0.1 %. The vapor pressures of isobutane and isopentane were also measured from (260 to 360) K. The uncertainty of the vapor pressures was estimated to be less than 500 Pa. The measured vapor pressures were correlated using a Wagner-type vapor pressure equation. The critical pressure, normal boiling point and acentric factor were then determined from the vapor pressure equation. Comparisons with the predictions of equation of state as well as experimental results are included.
The speed-of-sound data was measured in gaseous R600a, R744 and binary mixtures of R600a/R744 with R600a mole fractions of x1=0.47 and x1=0.26 along three isotherms from (310 to 330) K and at pressures up to 1000 kPa using a cylindrical resonator. The CO2 sample was obtained from Beiwen Gas Corp. with a stated mole purity of 99.995%, and the isobutane sample was obtained from Kedi Gas Corp. with a stated mole purity of 99.99%. The cylindrical resonator length and radius were calibrated with pure argon. The pure longitudinal frequency modes (200), (300) and (400) were used to calculate the speed of sound. The perturbations from the thermal and viscosity boundary layers, the shell motion, the fill duct and the vibration relaxation were considered and corrected in the frequency measurements. The experimental uncertainties in the temperature, pressure and speed of sound were estimated to be less than 5 mK, 200 Pa and 0.02%, respectively. The acoustic virial coefficients were deduced from the speed of sound data. The second virial coefficients were then obtained from the acoustic virial coefficients and the square-well intermolecular model.
The physical parameter for the so called Biologically Active Points most documented in the literature is the electrical impedance. These points seem to have higher electrical conductance than their surrounding points. The stimulation of these points up to now is made not only mechanically and electrically but also optically (laser acupuncture). As far as we know, few references about optical properties of BAP’s have been published in the scientific literature. We evaluated by optoacoustic technique, some skin points along the PC acupuncture meridian in the forearm region around PC5 and PC6. The measurements were performed each 0.5 cm from the wrist to complete 21 measurements (10 cm), using a Q switch NdYAG laser of 1064 nm wavelength, 5 Hz repetition rate, 9 ns pulse duration and below the security international limits for IR radiation for human tissues. The results were compared with those from a similar “line” parallel to the meridian, one centimeter toward the internal part of the forearm. We find a slight relative increment in absorption around one meridian region which could be associated with an acupuncture point but the same case is found in the non meridian skin line non associated with any acupuncture structures. Taken into account the normal variability of the skin absorption and dispersion, we can not conclude that such points are optically special.
The viscosity of simple, low-molecular-mass liquids is usually assumed to be independent of shear rate or shear stress. For certain types of tribological contacts, this assumption is no longer useful. These concentrated contacts are formed between the counterformal surfaces of machine elements made of high modulus materials. The films of liquid used to lubricate these contacts must flow under very high pressure, of the order of 1 GPa, in order to separate the surfaces. The shear stress applied to the liquid is of the order of 10 MPa. Analysis of the films requires that the viscosity under these conditions be known. A technique will be described for the measurement of viscosity at the pressure and shear stress of concentrated contact films. This technique has evolved in the author’s laboratory over about thirty years. Major difficulties include passing mechanical and electrical information across the high pressure boundary and the removal of the heat of viscous dissipation.
Description of Thermophysical Properties of Multi-Component Mixtures Employing Virial-Based Mixing Rules (VBMR)

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The last several decades have witnessed the development of a number of high fidelity methods for describing thermophysical properties of pure substances in condensed phases. They include corresponding states techniques and component-specific correlations, as well as statistical thermodynamics approaches. However, the science for describing mixtures has consistently trailed behind, often being limited to ideal mixing or similar formulations. For example, the mixing rules (typically implemented in process simulators) for liquid viscosity and thermal conductivity, are the Kendall-Monroe and Li correlations, respectively. While the attractive feature of such mixing rules is that they do not require interaction parameters (IP's), their downside is that they do not allow IP's, even when appropriate. In many applications, they incorrectly predict only a small deviation from ideal mixing, often with incorrect sign. Thus, while these mixing rules perform reasonably for hydrocarbon systems, their efficacy for non-ideal systems is questionable. The state-of-the-art is the Redlich-Kister correlation (RKC), which can incorporate additional higher-order terms to improve the fit of data with higher precision. It is often the correlation of choice for the applied thermodynamics research community, and has been successfully applied to precisely correlate a variety of thermophysical properties for binary mixtures. However, the RK correlation does not naturally extend to multi-component systems. This investigation draws upon the exact mathematics of mixing rules established for virial coefficients of gases. Perturbations from ideal mixing are modeled akin to successive terms in the virial expansion, resulting in the name “Virial-Based Mixing Rules” (VBMR). Each perturbation reduces to zero for pure components, and adopts the composition order of the corresponding virial coefficient it represents. For example, the first perturbation represents the second virial coefficient and implements a quadratic mixing rule, while allowing one adjustable binary interaction parameter. The next term employs cubic mixing and allows multiple interaction parameters, including a ternary interaction parameter which may be fine-tuned for ternary and higher mixtures. All interaction parameters are initialized to zero. Applying the VBMR methodology, Sen and co-workers have recently demonstrated excellent results for the correlation of several thermophysical properties for a number of binary liquid mixtures, including density, enthalpy, and viscosity. In this investigation, the VBMR methodology is extended to ternary (and multi-component systems), yielding non-zero ternary (and higher-order) interaction parameters accounting for three-body interactions, without compromising the goodness-of-fit for binary constituents. Comparisons are made with RKC, emphasizing how the VBMR naturally extends to multi-component systems, while the RKC does not. The VBMR model separates the temperature dependence of pure component and interaction parameters. This is postulated as a key reason for the smooth as well as weak temperature dependence of the interaction parameters. By contrast, the temperature dependence of model parameters for the RKC is often significantly jagged. This investigation implements and demonstrates the smooth temperature dependence for several binary and multi-component mixtures.
Raman scattering is not only applicable for structural characterization of molecular configuration and conformation in chemistry, but also relevant to physical properties of materials, such as temperature and stress. Thus information about temperature of specimen can be evaluated from intensity, Raman shift and linewidth of Raman signals. This provides the theoretical foundation for characterizing temperature by Raman scattering. In this work, a brand-new time-domain differential Raman (TD Raman) technology is developed to measure the thermal diffusivity of materials. The TD Raman technology uses a variable pulsed laser to heat the specimen and probe the temperature variation based on the principle of Raman thermometry and transient electrothermal (TET) technique. To evaluate this technique, silicon tipless cantilevers are used to conduct the experiment. A silicon tipless cantilever is heated by laser pulses and then Raman scattering spectrum of the specimen is collected. First of all, we develop a physical model to relate the accumulated Raman signal to the instantaneous Raman emission with temperature-dependent intensity, Raman shift, and linewidth. Then we develop a physical model to determine the thermal diffusivity of the cantilever by fitting curves of normalized Intensity and Raman shift against time. Sound agreement is obtained between the measured thermal diffusivity and the reference value. The TD Raman technology provides a very promising noncontact technique to measure the thermal diffusivity of materials without need of the temperature coefficients of Raman signals.
Liquid crystals are the phase in the state between solid and liquid phase. There are many different types of liquid crystal phases depending on the molecular orientational and positional order. The molecules exhibiting liquid crystal phases have the anisotropic shape such as rod-like and disk-like structure. The macroscopic structure of liquid crystal phase is strongly influenced by the collective behavior of these molecules. Therefore the study at the molecular scale is very important. When the phases are consisted of chiral molecules with rod-like structure, the chirality sometimes causes the molecules to arrange themselves in a twisted way. They are called chiral liquid crystal phase and getting a lot of attention recently. Many characteristic structure induced by this chirality were reported, e.g. the cholesteric phase (N*), the smectic C* phase, the blue phase (BP I, BP II and BP III) and the twist grain boundary phase (TGB). However there is relatively little study about the relationship between the molecular chirality and high-dimensional structure. In this research, Monte Carlo simulations were performed to investigate the phase transition of chiral liquid crystals. In order to describe chiral liquid crystal, we use chiral Gay-Berne potential developed by R. Memmer[1].

References

The flow properties of blood are an important factor in the evaluation of blood disease on the medicine, but the method of viscometry and the data collection are not so easy. In particular, Human arterial blood is so difficult practically. This study has been described on the viscosity measurement and their evaluations for horse arterial blood. A compact-sized falling needle rheometer with quick operation and automatic flow analysis has been developed for viscometry of blood, and the relationship between the apparent viscosity and physical properties of blood have also been evaluated. Measured flow properties of blood are evaluated as a flow curve showing the relationship between the shear stress and shear rate. Observed flow curves of bloods show three typical fluid regions, these are, the Non-newtonian fluid region for a low shear rate range, the transition region and the Newtonian fluid region for a high shear rate range. Flow properties of blood in the Casson fluid region and the apparent viscosity in the Newtonian fluid region are measured, and they are compared between horses. A non-linear relationship between the hematocrit value, that is, the volume percentage of red corpuscles in the horse arterial blood, and the apparent viscosity are observed. Finally, Flow properties of other mammalian bloods including horse blood are discussed on the effect of hematocrit values to blood viscosities.
The key issue of accurately measuring surface temperature is to maintain a hot surface without reflection of hot environment. We used the integral blackbody technique to solve such problem. A emissivity measurement apparatus at high temperature is building up based on this method at NIM. The apparatus consists of an air cylinder and a water-cooled copper cylindrical rod extension, it connects the air cylinder and a high strength graphite rod extending into a graphite tube furnace. Because of the reflections from the cylindrical section, the resulting cavity radiates as a blackbody. After the air cylinder rapidly moves the specimen to the end of the heater tube, the specimen exposes to the cooling environment. The ratio of the free standing radiation to the blackbody radiation is calculated, and it can be measured as the emissivity at high temperature[2].
Modelling of the Specimen Temperature Drop of a High Temperature Emissivity Measurement Facility

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Accurate emissivity measurement at high temperature, especially above 1000°C, plays a vital role in the high temperature processing, such as thermal modelling and radiation thermometry. However, it’s extremely difficult to achieve a satisfying result, and very few results were published before [M. Ballico, G. Neuer, G. Herdrich, M. Modest]. The key issue of accurately measuring surface temperature is to maintain a hot surface without reflection of hot environment. We used the integral blackbody technique to solve such problem. A emissivity measurement apparatus at high temperature is building up based on this method at NIM. The apparatus consists of an air cylinder and a water-cooled copper cylindrical rod extension, it connects the air cylinder and a high strength graphite rod extending into a graphite tube furnace. Because of the reflections from the cylindrical section, the resulting cavity radiates as a blackbody. After the air cylinder rapidly moves the specimen to the end of the heater tube, the specimen exposes to the cooling environment. The ratio of the free standing radiation to the blackbody radiation is calculated, and it can be measured as the emissivity at high temperature [C. Liller]. In this study, the temperature drop of the specimen during the moving of the cylinder is simulated in order to achieve the accurate emissivity when the sample is exposed to the cooling environment. In this paper, a FEA model is used to model the thermal process and the results will be reported.
Spatially Resolved Acoustic Spectroscopy (SRAS): 
from Surface Acoustic Waves Velocities to Crystallographic Orientation

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The microstructure and properties of a material determine its characteristics such as strength and stiffness. The laser ultrasonic technique spatially resolved acoustic spectroscopy (SRAS), which generates surface acoustic waves (SAW) thermoelastically, is a robust and rapid method to quantitatively measure the velocity of SAW propagating on the material's surface. The topographic map of velocity is obtained and shows the contrast of grains. We developed a forward model which predicts the SAW velocity for all the combinations of plane and SAW propagation direction of a material based on its elastic constants. The purpose of the work presented is to determine the orientation of the crystal or grain according to the measured SAW velocities in a limited number of directions. A search algorithm, termed the overlap function, solves this inverse problem and is tuned for SRAS results which present data as a velocity surface spectrum. The orientation results of a range of industrial materials, such as nickel-based alloys, titanium-based alloys and stainless steels, have been presented with comparison with electron back-scattered diffraction technique. We discuss the influence of number of directions in the SAW velocity measurements which affect the accurate determination of the planes. The implementation of this technique utilizes the triangular relation of three elements – elastic constants, crystallographic orientation and SAW velocities – by knowing any of the two, the third one can be achieved. However, it is possible to determine the elastic constants by SAW velocities on multigrain materials without knowing the orientation of grains. The feasibility study of cubic structure materials are demonstrated.
Carbon dioxide capture and storage (CCS) is one of the most important technologies to prevent global warming caused by carbon dioxide. Captured CO2 streams from flue gas may include impurities such as nitrogen, water, sulfur dioxide, nitric oxide, oxygen, argon, methane, and hydrogen sulfide. Impurities in the CO2 streams have significant impact on thermodynamic and transport properties, for example, corrosion rate and hydrate formation condition can be different from pure CO2. For such reasons, it is required to have accurate information about the effect of impurities on thermodynamic properties of CO2 in order to develop proper CCS processes. There have been very little studies about the effect of nitric oxide as compared with other impurities such as nitrogen, methane and water. In this study, Hydrate-containing phase equilibria of nitric oxide was experimentally determined in liquid-hydrate-vapor (Lw-H-V) three phase line at the pressure ranging from 10 to 14 MPa. Isobaric dissolution temperatures of formed hydrates were measured and reported for predetermined loading compositions. The measurement result shows that the hydrate-containing phase line of nitric oxide is shifted to lower temperature at the same pressure due to reaction of nitric oxide with water.
Low-quality crude oil can be upgraded to high quality by removing naphthenic acids which may cause corrosion of equipment and deactivation of catalysts in cracking units. Previous studies show that techniques such as neutralization, esterification, and decarboxylation can be applied to remove naphthenic acids. However, these methods cause other problems such as formation of naphthenic salts/water emulsions and requirement of catalysts with harsh reaction condition. In this study, solvent extraction method was investigated and solvents with high extraction capability, proper physical properties was to be sought. For solvent screening, computer tools such as TDE 8.0 (NIST), ProCAMD (Technical Univ. of Denmark) and COSMOtherm (COSMOlogics GmbH) were used to scan over the list of solvent candidates. After selection of a few solvent candidates, extraction performances were compared by extraction experiment using pseudo-crude oil mixtures. Pseudo-crude oil mixtures were prepared by adding predetermined weight of naphthenic acid to diesel oil. The prepared mixtures were extracted using selected solvents for 2 hours at the temperature of 333.15 K and atmospheric pressure. The performances of solvents were evaluated by acidity determined from titrations of extracted pseudo crude oil. The results shows that several candidate solvents can remove naphthenic acids to commercially meaningful level.
Comparison of Properties Calculation Methods for Design of Carbon Dioxide Transportation

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Process simulation tools are widely used for the design of carbon dioxide capture and transportation processes. Appropriate selection of calculation methods and proper use of parameters are crucial for the success of design for such processes. Flue gas from various source contain different level of impurities in carbon dioxide streams. Impurities such as nitrogen, oxygen, methane, NOx and SOx affects the properties and phase equilibrium of carbon dioxide streams. In this study, comparison of performances in calculations for properties and phase equilibrium has been investigated for various equation of state models such as cubic, SAFT and GERG. Especially, VLE calculation for system containing sulfur dioxide and nitric oxide was highlighted due to limited study for these systems. For several systems, suggested binary interaction parameters are reported for use in the commercial simulation software such as Aspen Plus. This evaluation study is expected to provide guidelines for establishing thermodynamic package for design of carbon dioxide transport processes.
Breast cancer is a predominant cancer worldwide among women. To address this problem, a considerable scientific effort has already been going on round the globe seeking early detection of the disease. Many optical spectroscopy techniques have also been experimented to detect breast cancer early and with reduced costs. Studies based on photoacoustic spectroscopy have shown steady growth and demonstrated enough capabilities to detect the disease early. With the aim to detect breast cancer early, tumor progression in nude mice as xenograft model was studied using a pulsed laser induced photoacoustic spectroscopy. Tumor tissues were extracted from the nude mice xenografts at different time points (10th, 15th & 20th day) post MCF-7 cells injection and the corresponding photoacoustic spectra were recorded at 281nm pulsed laser excitations. There were 144 time domain photoacoustic spectra recorded from 36 tumor tissues belonging to 36 animals, 12 each to the three time point groups (10th, 15th and 20th day post injection). The spectra were then Fast Fourier transformed using MATLAB algorithms for further analysis. The spectral comparison of the inter-day group of animals have shown a distinct pattern in the intensity of peaks at 5.93 x103Hz, 15.9 x103 Hz, 29.69 x103 Hz and 32.5 x103 Hz respectively indicating that these frequencies are more sensitive towards tumor development. Further discrimination analysis of the data also indicated a clear variation in the spectral patterns of the samples belonging to different time point groups under study highlighting the sensitivity of the technique in identifying tumor development and growth. The outcomes of the study clearly demonstrated the usefulness of the technique in assessing tumor development and growth which may have clinical implications.
The International System of Units and the Big Revision Coming in 2018

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In November 2014 the 25th meeting of the General Conference on Weights and Measures (CGPM) encouraged all parties concerned to complete work on a major revision of the International System of Units (SI) in time for approval by the 26th CGPM meeting in 2018, assuming that “the amount of data, their uncertainties, and level of consistency are deemed satisfactory.” Although similarly hopeful statements have been made over the years, there is at last general agreement among those involved with producing the required data that the 2018 target will be achieved. We are approaching the end of a long and historic effort to revise our system of units. It is therefore timely to discuss how the SI will change and what the changes will mean for scientists and engineers presently making accurate and precise measurements expressed in SI units.

Much of the SI will not change perceptibly: it will have the same seven base units as today and the magnitudes of these units will also be the same. However, the definitions and primary realizations of the units will henceforth better suit contemporary science and technology. The kilogram, most notably, will no longer be defined by the mass of a unique cylinder of platinum-iridium dating from 1889. (Has its mass been stable for 125 years?) Instead, the kilogram will be defined in terms of a fixed value of the Planck constant (SI unit: J s = kg m²/s) and the present definitions of the second and metre. A similar treatment is in store for three other base units: the ampere, the kelvin, and the mole. I will review some of the key issues still under discussion, experiments that make this program possible, and how the revised SI units will be realized in practice.
The analysis of hydrocarbon fuels by \(^1H\) and \(^{13}C\) nuclear magnetic resonance (NMR) spectroscopy will be discussed. NMR spectroscopy is particularly useful for the analysis of complex hydrocarbon mixtures for two reasons. First, several important structural moieties (such as olefins or aromatics) are segregated into specific spectral regions. Second, spectra can be collected in such a way that the spectrometer is equally sensitive to all \(^{13}C\) nuclei (or to all \(^1H\) nuclei). As a result of these two features, NMR spectroscopy readily provides the mole fractions of various classes of hydrocarbons (such as aromatics and linear alkanes) in a sample without the need to calibrate. NMR spectroscopy also gives easy access to other average properties for the components of each fuel sample, such as the extent and type of alkane branching. Such information is useful for the development of realistic fuel surrogates and reliable thermophysical models. The advantages and disadvantages of NMR spectroscopy will be illustrated by spectral analyses for two types of fuel samples: gas turbine fuels (i.e., jet fuel) and hydrotreated renewable diesel fuel. A discussion of sources of uncertainty in such an analysis will be included. Finally, a comparison of the results obtained by NMR spectroscopy to analyses by GC-MS and GC-FID will be discussed.
The subject of water, and particularly metastable water, has perennially been a focus of controversy amongst physicists and physical chemists. Both thermodynamic and relaxation kinetics properties seem to obey power laws in their temperature dependence, implying a critical behavior of some sort, but whether the power laws imply the existence of a true critical fluctuation zone or only the existence of a spinodal stability limit of the phase under study, is not yet clear. The distinction depends on whether the critical zone lies at positive or negative pressures (1). The most convincing account of the available data to date locates the critical point at weakly positive pressures (2), but shows such sensitivity to parameter choices that negative pressure values are not excluded. In one possible scenario, known as the "critical-point-free" scenario, the critical zone is supposed to lie at such large negative pressures that it would merge with the better understood spinodal limit of the liquid with respect to cavitation, i.e. the tensile limit. Indeed this is the scenario most closely according with all the empiricists' extrapolated equations of state (1). In this talk we consider the things we know, and the things we need to know, but at this time, don't. We discuss the most recent developments that promise new information including ultrafast heating rate studies of heat capacity (3), crystallization kinetics, and particularly studies performed at negative pressures (4, 5) where crystallization of ice seems to become less pre-emptive of the interesting behavior (5). Finally we consider some findings on new types of aqueous solutions in which the behavior remains dominated by the anomalies of water, but now the interesting properties are manifesting themselves in a zone where crystallization kinetics are slow and crystallization can be bypassed completely (6).

References

Ideal-gas thermodynamic properties of urea computed using experimental vibrational spectrum from matrix-isolated urea sample [1] and assuming C\textsubscript{2v} symmetry were found in good agreement with entropy data observed experimentally [2]. The reported low-frequency absorption band of 227 cm\textsuperscript{-1} assigned to NH\textsubscript{2} group inversion and mainly responsible for the observed agreement, however, is not confirmed by the subsequent microwave study and quantum-chemical calculations at the MP2/6-311++G** level [3]. Non-planar stereoisomers of urea with C\textsubscript{2} and C\textsubscript{s} symmetry were identified. The lowest vibrational frequency for the most stable (C\textsubscript{2}) structure was predicted to be 385 cm\textsuperscript{-1}, much higher than obtained in matrix isolation experiments. In this report, we present new quantum chemical calculations and detailed statistical-mechanical analysis aimed to reconcile the experimental and theoretical findings. A particular consideration is given to suggested anharmonic effects [3] of NH\textsubscript{2} inversion modes.

References

Determination of Phase Equilibria for the Mixture (CO₂ + CH₄)

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High-pressure phase equilibrium data are often complex and difficult to predict and it is necessary to obtain some experimental data. The electric permittivity or dielectric constant is a physical property that can be defined as the electric polarization acquired by the molecules of a substance as a result of the induction generated by an electromagnetic field. It is an extensive property which depends on temperature and pressure ε(p,T). Based on this property has been developed a measurement technique which consists of a cylindrical resonant cavity that works in the microwave band; a sapphire tube with the sample is located inside this cavity. The resonant modes of cylindrical cavity depend on the electrical properties of the sample. For example, a liquid sample is maintained at constant temperature and the pressure is decreasing until the first bubble occurs, this phase transition presents a discontinuity in the electric permittivity and therefore in the resonant modes of the cavity. With the reverse procedure it is possible to measure the dew point. With this technique, the equilibrium data of fluid mixtures at high pressure are measured applying the synthetic method. This technique can be an alternative to the traditional visual synthetic method. The technique was checked and it has been used for measuring the phase behaviour of the binary mixture (CO₂+CH₄) which results are presented.

Acknowledgments

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Experimental Viscosities and Densities of CO2-Crude Oil Mixtures Up to 453 K and High Pressures Using a Vibrating-Wire Viscometer and Vibrating-Tube Densimeter

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With the increasing maturity of conventional oil resources and limited volumes of new conventional resources to replace production, attention has been focused on viscosity reduction to enhance oil production from brown-field reservoirs by the injection of light gases such as CO2. Also, viscosity plays a significant role in managing and controlling injection of CO2 into depleted oil reservoirs or saline aquifers for the purpose of carbon sequestration. In this study, an experimental measurement on viscosity and density of mixtures of crude oils and CO2 was performed using accurate technique such as vibrating-wire viscometer. However, for viscosity measurements involving crude oil using vibrating-wire viscometer, asphaltene precipitation and deposition can be a problem. This problem can have effects on the viscometer sensor, flow lines and fittings and introduced a significant error that can affect the accuracy of the results. Therefore, the ASTM recommended procedure (ASTM2007-80) for separating asphaltene was modified to obtain representative crude oils free of asphaltene. The range of temperature was (273.18 to 453) K while that of pressure was (0.1 to 130) MPa. The experimental data will be used for modelling of the viscosity of crude oil + CO2 at elevated pressure and temperature using appropriate model for improved prediction of the CO2-crude oil mixture under persistently changing conditions of composition, pressure, temperature and conditions common with reservoir fluids.
Ph-Driven Reversible Aqueous Biphasic Systems Composed of Ionic Liquids

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Recently, a large interest has been devoted to the exploitation of dynamic and reversible biphasic systems constituted by ionic liquids (ILs) [1]. It was previously demonstrated that mixtures involving ILs and other solvents can be switched between the homogeneous regime and a two-phase system either by a temperature-driven phenomenon or by adding CO₂/N₂ [1]. These systems have shown to be remarkable in the selective separation of several value-added compounds, such as proteins [1]. Amongst the liquid-liquid extraction techniques, aqueous biphasic systems (ABS) constitute a “greener” and more benign and biocompatible option since they are mainly composed of water (ca. 50 wt%). Furthermore, these systems can lead to the complete extraction of a wide variety of compounds and to high concentration factors [2]. In addition to all the advantages and enhanced performance of IL-based ABS, their switchable character between a two-phase and a homogeneous regime was not previously attempted. The major goal of this work consists on the exploitation of switchable IL-based ABS triggered by a pH-dependent phenomenon. A large array of ABS, obtained by the combination of potassium citrate with different ILs, was initially investigated by the determination of their ternary phase diagrams at different pH values. The first set of reversible IL-based ABS was ascertained by the addition of citric acid or potassium hydroxide and through the organic salt speciation. Their reversibility behaviour was demonstrated for at least 3 times. In addition to IL-salt mixtures, polymer-IL-based ABS were also investigated while reaching their switchable behaviour through the IL anion speciation. Finally, these ABS were explored as fractionation techniques for amino acids and peptides.

Acknowledgements

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References


Polycyclic Aromatic Hydrocarbons (PAHs) are common compounds consisting of two or more fused aromatic rings. The interest in these compounds is twofold: a) they are pollutants that can be found mainly in soils and sediments as a result of fuel combustion; b) they represent the pathway from benzene to carbon-nanomaterials. The development of novel bioremediation processes to reduce the risk of exposure to these compounds is limited by their very low solubility in water, which declines with the increasing number of aromatic rings [1]. To date many works on surfactant micellar solubilization of hydrophobic compounds have used conventional surfactants [2,3]. Ionic liquids are known as designer solvents with solubility behaviour that can be tuned through changes in both cation and/or anion. Moreover, they can also present surfactant behaviour that enhances their potential as co-solvents. In this context we have used ionic liquids as solubilisers of hydrophobic PAHs. The PAHs solubility behaviour was mapped in all range of concentrations of ionic liquid in water, from more diluted solutions to pure ionic liquids. Several distinct families of ionic liquids have been used in this work. As expected the best results in aqueous solutions appear with ionic liquids that present surfactant-like behaviour. The model compounds chosen were naphthalene, anthracene, phenanthrene, pyrene and coronene. HPLC was used to measure the solubility of the PAHs in both pure ionic liquid as well as ionic liquid aqueous solutions. Ab-initio calculations and Molecular Dynamics simulations have been used as valuable tools to unravel the interactions between the aromatic moieties and the selected surface active ionic liquids.

References

ILThermo Version 2.0: Archival Storage and Retrieval of Thermophysical Properties for Ionic Liquids

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Originally developed under the auspices of IUPAC (Project 2003-020-2-100), ILThermo [1] (http://ilthermo.boulder.nist.gov/) is an archival database of experimental thermophysical properties of ionic liquids and mixtures that contain them. The original version had its public release in 2006. In 2013, Version 2.0 [2] was released by the Thermodynamics Research Center of the NIST Material Measurement Laboratory, Applied Chemicals and Materials Division. ILThermo is a web-based open-access database that provide up-to-date information on publications of the results of experimental studies of ionic liquids, including numerical values of thermophysical and thermochemical properties, chemical structures, measurement methods, sample purity, critically evaluated uncertainty of property values, as well as other significant measurement details. In the intervening nine years since its public release (July, 2006), NIST has continued to populate ILThermo with information derived from recently published articles. While ILThermo’s data population has doubled twice, at the same time this work has seen significant challenges. The challenges that are central to this effort include: high volume of relevant articles; wide dispersion of published articles; wide variety of possible cations and anions; inconsistent compound nomenclature and abbreviations; and, poor availability of compound registry numbers. We describe how those challenges were addressed and solutions that were developed. In addition, NIST has seized upon new opportunities to broaden the scope and functionality of on-demand data evaluation that is feasible within the ionic liquids archive. Such on-demand evaluations are carried out with the application NIST ThermoData Engine (TDE), which is a software implementation of the concept of dynamic data evaluation. We describe key opportunities that include experiment planning and product design for ionic liquids. Planning tools would be considered most useful when they help experimentalists prioritize their measurements on ionic liquids. Such outcomes of planning are meaningful only if the underlying evaluation for a given property takes into consideration their uncertainties, their measurement ranges, and essentially all published values. Experiment planning tools will answer queries such as What should I measure that will have a significant impact? In addition, process engineers need product design tools that help identify candidate ionic liquids that have a set of desired properties. Product design tools will answer queries such as Which ionic liquid has the right thermophysical properties for my process application? We discuss NIST’s approach to these research opportunities, beginning with development and a recent release of TDE software and leading to future developments of TDE. Research will be necessary to extend TDE, presently applicable to molecular compounds, to ionic liquids and mixtures that contain them.

References

The Van der Waals Ten Commandments for the Designers of Cubic Equations-of-State

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The reading of the Van der Waals (VDW) 1910 Nobel Prize Lecture reveals the hindsight and foresights of the VDW theory of cubic equations of state for the design of a Substance-Based Cubic Equation-of-State, which is in accord with the VDW objective. A correct reading of the VDW Nobel Prize Lecture reveals some Do's and Don'ts and their consequences led the author to the following itemized Van der Waals Ten Commandments for Cubic Equations-of-State (they summarize Designers’ obligations to cubic equations and to the VDW theory), which begins with Oh the Faithful:

- Be Loyal to the VDW Cubic Form of Attractive and Repulsive Expressions
- Be Loyal to the VDW Ultimate Objective: Construct A Substance-Based Cubic Equation
- Be Loyal to the VDW Asymptotic Critical Volume-Limit: Weak-Point of VDW Theory
- Be Loyal to the Four Properties of the VDW Theory of Cubic Equations of State
- Be Loyal to the VDW Empirically-Based Molecular Parameters for Reformed Equations
- Be Loyal to the VDW Critical Point as Limit of Phenomenological Gas-Liquid Transition
- Be Loyal to the VDW Defined Gas-Constant for Unifying Caloric and Transport EOS
- Be Loyal to the VDW Continuity of Gas and Liquid States for Temperature Functions
- Be Loyal to the VDW Constraining Temperature Parameters to a(T) and b(T)
- Be Loyal to the VDW Corresponding States Principles for Generalized Property Charts
As yet, fluids have refused to be boxed into the two-parameter cubic equation of state that Van der Waals (VDW) prepared for them. But, the VDW 1873 theory specified four properties for determining the $P$, $v$, $T$ relation of a substance, including the fluid gas-liquid critical point, which is in accord with the four critical constraint criteria used to specify those properties for the VDW theory of cubic equations of state and that also is in agreement with the four parameters stipulated by the theory of cubic polynomial equations of state. Since the VDW theory has acknowledged molecular size and molecular attraction into the 1873 equation, the possibility of including two inspired parameters into the VDW 1873 theory can be inferred from the 1910 Nobel Prize Lecture in which VDW categorically rejected non-molecular based and non-physically meaningful empirical parameters into the 1873 theory. By relating the empirical parameters ($\alpha$, $\beta$) of the Lawal-Lake-Silberberg (LLS) equation to the microscopic force-parameters derived from the statistical mechanics energy potential functions and performing perturbation and other sensitivity analysis; the sensitivity of the derivatives of the structural parameters ($P_c$, $Z_c$, $T_c$) and the sensitivity of the derivatives of second, third and fourth virial coefficients with respect to $\alpha$ show non-linear trend with $\alpha$-parameter and thus, $\alpha$ replicates structure of pure substances in the configuration of the LLS equation. Similar analysis of the derivatives of the critical volume ($V_c$) and Boyle temperature ($T_B$) with respect to $\beta$ show non-linear trend with $\beta$-parameter and thus $\beta$ reflects shapes of pure substances in the configuration of the LLS equation. The empirically-based molecular parameters ($\alpha$, $\beta$) bring the VDW 1873 equation in conformity to the stipulated shapes of the potential energy and length scale of the statistical mechanical potential functions and reconcile the VDW theory with liquid-phase properties and gas-liquid critical point.
This poster is dedicated to my teacher and mentor of 33 years, while he is not going to be at this 19th Symposium on thermophysical properties, his interest is always in thermodynamics, both measurements, correlations, estimations and predictions of fluid properties of interest to the chemical and petroleum engineers. He graduated from UT Austin and all his degrees are in chemical engineering (his Advisors were the late Chairman of Chemical Engineering Department, Dr. Kobe and the former Dean of the College of Engineering, Dr. John McKetta). After a brief stay at Mongolia Oil Company (now Mobil Oil), he spent the rest of his career at UT (1959-2010) and became the Associate Director of the Texas Petroleum Research Committee, with residency in the old Petroleum Engineering Building. During my era at UT, he was my Graduate Advisor and the Chairman of the Graduate Study Committee in the PE Department. I had daily consultation with him during the development of K-value correlations and the improved cubic equation of state (which I have affectionately named the Lawal-Lake-Silberberg (LLS) cubic equation). I can surely see his influence in my post-graduate career. It is his invocation that is an impetus for me to seek the copy of the 1890 English Translation of the Van der Waals dissertation from the Library of Congress in DC and seek to read the Speech of the 1910 Nobel Prize Lecture of Van der Waals; and his influence made me to engage on the solution to the VdW cubic equation of state. I was his last PhD Trainee and graduate assistant and he co-Chair my PhD Project with Dr. Larry Lake of PE Department. I would like to share my thought with those who are attending the 19th Symposium on thermophysical properties and watch me perform brilliantly in the abstracts submitted for posters and presentations and I hope you will share some of those thoughts with colleagues and your students. Here are my recollections (or axioms) of working as graduate student with Dr. I. H. Silberberg:
A theoretical analysis of NIR photon flux through radiative recombination and thermal emission through nonradiatively recombining excess minority carriers under modulated super-bandgap laser excitation in solar cell will be presented. The developed optoelectronic and thermoelectronic expressions allow the noncontact determination of solar-cell electrical parameters such as dark saturation current, ideality factor, solar conversion efficiency, fill factor, photogeneration current density and maximum power photovoltage based on statistical camera pixel distributions of carrierographic or thermographic images obtained over the entire solar cell surface area. The reliability of the LIC and LIT evaluated parameters was confirmed by means of traditional electrical measurements. It is shown that carrierographic images have higher spatial resolution and sensitivity to local distribution of parameters than the respective thermographic images. All-optical non-contact-generated current-voltage (I-V)-equivalent characteristics of multicrystalline solar cells will be presented using laser intensity scans in lieu of photovoltage variation changes through external load resistance changes, and the associated collected radiative recombination flux in lieu of electrical current.
One hundred years have elapsed since the publication of the famous ethylammonium nitrate study by Paul Walden, probably one of the most long-known Ionic Liquid (IL). Even so, only recent years witnessed a greater interest on this class of medium, especially when it was realized that they could advantageously replace traditional organic fluids due to their singular properties. Moreover, the possibility of “designing” their structure to achieve the desired properties for a specific application also boosted their use in industrial applications. In this work, we have synthesized three bistriflimide ammonium-based ILs with similar size but with distinctive functional groups in one single alkyl chain, namely \([\text{N}_{21130H}][\text{Ntf}_2]\), \([\text{N}_{211201}][\text{Ntf}_2]\) and \([\text{N}_{2114}][\text{Ntf}_2]\). The aim of this study is to evaluate the impact of these distinctive functional groups on the thermophysical properties of these ILs, such as density, viscosity, conductivity and refractive index and on their fluid phase equilibria behavior with molecular solvents such as ethers, alcohols, diols, and water. Lower critical solution temperatures (LCST) type phase diagrams were observed for the mixtures of these ammonium based ILs with ethers, while upper critical solution temperature (UCST) type phase diagrams were reported for all the other systems. The miscibility behavior of ILs with different solvents strongly depends on the number and position of the functional groups and the size of the alkyl chain of the solvent, as well as, the functional group of the IL. The experimental results also show that for these almost equal sized ammonium based ILs different physical properties can be obtained through a particular exchange of the functional group of one single alkyl chain. Molecular dynamics simulation will be used as a tool to help on the understanding the observed behavior.
A non-destructive quantitative lock-in thermography imaging technique using a mid-infrared camera for evaluation of the absolute values of thicknesses and thermophysical parameters of industrial coated samples from images obtained in a sequence of laser beam modulation frequencies has been developed. Analytical studies of associated photothermal radiometry frequency scans were undertaken to measure the values of several geometrical and thermophysical parameters of a metal substrate with a deposited thin coating layer. The quantitative multi-parameter results were studied with regard to measurement reliability (uniqueness) and precision using two independent best-fit programs. The lock-in thermography technique was further extended to thermal-wave radar imaging, a modality found to exhibit better contrast and much faster image acquisition rate, very desirable attributes for industrial inspection and manufacturing quality control.
Densities and Refractive Indices of solutions of potassium bromate (KBrO₃) have been studied in water and 0.1%, 0.2%, 0.3%, 0.4% and 0.5% (w/v) aqueous solution of KNO₃ with temperature in the range T = 298.15°K, 303.15°K, 308.15°K, 313.15°K. The data obtained is utilized to determine Specific Refraction (R_D) and Molar Refraction (R_M) of solutions. The values of Refractive indices, Molar Refraction (R_M) and Molar Polarisability (α) constant are found to be decreased with decreasing concentration of solute in solvent and these results are also interpreted in terms of interaction in salt solution. It has been verified that Molar Refraction is additive and constitutive property.
Densities and Refractive Indices of solutions of potassium bromate (KBrO₃) have been studied in water and 0.1%, 0.2%, 0.3%, 0.4% and 0.5% (w/v) aqueous solution of KNO₃ with temperature in the range T = 298.15°C- 313.15°C. The data obtained is utilized to determine Specific Refraction ($R_D$) and Molar Refraction ($R_M$) of solutions. The values of Refractive indices, Molar Refraction ($R_M$) and Molar Polarizability ($\alpha$) constant are found to be decreased with decreasing concentration of solute in solvent and these results are also interpreted in terms of interaction in salt solution. It has been verified that Molar Refraction is additive and constitutive property.
Simultaneous Measurement of Viscosity and Density with a Capillary Tube Viscometer: Preliminary results for CO₂, Hexanol, Nonane and Decane

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In this work, preliminary results of simultaneous measurements of dynamic viscosities and densities for CO₂, hexanol, nonane and decane are presented. The viscosity have been measured with a modified capillary viscometer designed and built to operate at pressures up to 40 MPa and temperatures up to 473.15 K. To increase the precision of the developed instrument, the density of fluids in study has been simultaneously determined (to the same conditions of viscosity measurements) with a calculated experimental uncertainty of the order of ±0.26 kg/m³. The dynamic viscosity and densities were measured at pressures up to 30 MPa and temperatures up to 353 K. The total uncertainties of the dynamic viscosity measurements were estimated to be less than 0.75%. The measured dynamic viscosities and densities were compared with data, predictions and correlations previously reported in the literature, where the differences between the literature and the measurements reported here are less than 0.6% for viscosity and less than 0.04% for density.
Phase Equilibria Prediction of Selected Hydrocarbon/Hydrofluorocarbon Mixtures

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Organic Rankine cycle (ORC) receives much attention for recycling low grade thermal energy, such as biomass, geothermal energy, and waste heat. Recent research shows that ORC systems using mixture as working fluid has better performance than that using pure working fluid, because of better temperature match between heat source and working fluid and less irreversible loss. Similar with ORC using pure working fluid, selection of working fluid also has great influence on cycle performance of ORC system using mixture as working fluid. And thermodynamic properties of mixture are fundamental and crucial for fluid selection and cycle design. Besides, the properties in the critical region are very important since research has shown that cycle efficiency increases as the evaporation pressure approaches critical pressure. Therefore, the main objective of this paper is to provide a good method to describe the vapor-liquid equilibrium (VLE) and single phase properties of mixture for hydrocarbon/hydrofluorocarbon, including mixture of R600, R600a, R601, R601a, and R236ea, R245fa. The main reason for choosing these mixtures is that they can compensate the disadvantages of each other and the mixture is more environmental friendly than the pure fluid. In this paper, crossover volume translation SRK(VTSRK) equation of state(EoS) we developed before was extended to hydrocarbon/ hydrofluorocarbon mixtures (R600/R236ea, R600/R245fa, R600a/R236ea, R600a/R245fa, R601/R236ea, R601/R245fa, R601a/R236ea, R601a/R245fa) combined with Vander Waals(VDW) mixing rule. The results predicted by crossover VTSRK EoS were compared with the experimental data for mixtures in the one and two-phase regions. Comparison results show that the crossover VTSRK EoS improved the description of thermodynamic properties, especially in the critical region. This lays a foundation for working fluid selection and cycle design of ORC.
Tabulation of Critical Viscosity and Critical Thermal Conductivity by Inverting the Parameters of Van der Waals Transport Equation

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The phenomenological similarity between the spinodal shape of the PVT and TηP graphs in which the positions of pressure and temperature are interchanged and the dynamic viscosity (η) or (thermal conductivity, λ) takes the position of molar volume in the Van der Waals theory of cubic equations of state has been accorded an hypothetical name, “Van der Waals theory of Transport Equation of State (VTEOS).” Such Van der Waals (VDW) spinodal shapes have been experimentally reported on fifty pure substances for dynamic viscosity and sixteen thermal conductivities of gaseous and liquid states. Since the critical point is the finite terminal-point of the gas-liquid phase transition in the VDW theory (as opposed to the Sengers theory of infinite thermal conductivity of Carbon dioxide) and experimentalists never measured the critical point of transport properties (viscosity, kinematic viscosity, thermal conductivity, thermal diffusivity, molecular diffusivity, Prandtl number, Eucken factor and dielectric constant), the technique of the VTEOS has not received as much attention as those of the non-equilibrium statistical mechanics reviewed by Millat et al., (1996) and other methods reviewed by Poling et al. (2001) and Green-Perry (2008). Since The Law of Corresponding States for transport properties depend on critical transport properties, the VDW phenomenological gas-liquid transition point provides the basis for estimation of rarely known and not easily measured critical properties. By establishing the reduced transport properties using VTEOS at the specified temperature and pressure of the experimental data, we back-out critical transport properties of the specified pure substances. By applying statistical averaging methods, a single value of critical viscosity or critical thermal conductivity is established for pure substances. By repeating the procedure for several pure substances, a tabulation of critical viscosity and thermal conductivity is provided along the basic data tabulated by Poling et al. (2001) and Christian Ihmels (2010).
Following carbon dioxide injection in deep saline aquifers, CO\textsubscript{2} dissolves in the formation brines forming acidic solutions that can subsequently react with host reservoir minerals, altering both porosity and permeability. The direction and rates of these reactions are influenced by several factors including properties that are associated with the brine system. Consequently, understanding and quantifying the impacts of the chemical and physical properties of the reacting fluids and their effect on overall reaction kinetics is fundamental to predicting the properties of the injected CO\textsubscript{2}. In this work, we present a thorough experimental study of the properties of different brine systems by varying ionic strengths and ionic species. The impact of these variables on rock-fluid chemical reactions is examined. Using a rotating disk technique, we have investigated the chemical interactions between CO\textsubscript{2}-saturated brines and carbonate minerals such as calcite and dolomite at pressures (up to 15MPa) and temperatures (up to 353K) – conditions pertinent to carbon storage. Kinetic parameters derived from the study are subsequently applied to our previously derived computer model.
New Class of Self-Buffering Ionic Liquid and Its Application for Separation of 1,3-Dioxolane From Its Azeotropic Aqueous Solution

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In this work we synthesized a new self-buffering and biocompatible ionic liquid, in which anion was derived from a commonly used biological Good buffer (GB), 4-(2-hydroxyethyl)-1-piperazinepropanesulfonic acid (EPPS) and cation was contributed from tetramethylammonium (TMA). The buffering action of this new synthesized Good buffer ionic liquid (GBIL) is confirmed by measuring its pH profile in aqueous solution. Moreover, the pKa values of the GBIL in water were determined experimentally at 293.2 K, 298.15 K and 308.15 K. It was also found that the presence of this new GBIL, [TMA][EPPS], in 1,3-dioxolane aqueous solution could induce liquid-liquid phase splitting. The influence of this new GBIL on the separation of 1,3-dioxolane from its aqueous solution has been investigated by measuring solid-liquid-liquid equilibrium (SLLE) and liquid-liquid equilibrium (LLE) data for the 1,3-dioxolane + water + GBIL system under atmospheric pressure and at 298.2 K. The experimental LLE tie-line data were correlated well with the NRTL model and their consistency has been confirmed by correlating the LLE tie-line data with the Othmer-Tobias equation. The experimental results also indicated that this new GBIL can be used as an attractive auxiliary agent to recover high purity 1,3-dioxolane from its azeotropic solution. A greener separation process is proposed in the present study. In comparison with the conventional inorganic salts, this new GBIL is a biocompatible, non-corrosive, and green compound.
Spectral Frustration and Spatial Coherence in Thermal Near-Field Scattering

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The thermal optical near-field in close proximity to a thermal emitter exhibits fundamentally distinct spectral, spatial, and coherence properties. Using thermal infrared near-field spectroscopy (TINS), we probe the electromagnetic local density of states (EM-LDOS), which is resonantly enhanced in the presence of molecular or polariton resonances. Using SiC as an example, we study the thermal spectroscopic response associated with its SPhP resonance and observe pronounced spectral frustration with variable red-shifts ranging from ~5 cm\(^{-1}\) to ~50 cm\(^{-1}\). While modest spectral shifts can be attributed to tip-sample coupling, we propose an effective medium change by the tip responsible for large shifts. In addition, we find an exponential distance dependence of SiC TINS which we attribute to the preferential scattering of the spatially coherent thermally-excited SPhP field. We have recently implemented laser heating of the tips which enables studies at higher temperatures and with stronger tip-sample coupling. We observe an extreme red-shift of the SiC spectrum of up to 55 cm\(^{-1}\), while the intrinsic molecular resonance of PTFE is unshifted, as expected. We extend these studies to the hyperbolic, van der Waals material hBN, and observe a strong peak at 1350 cm\(^{-1}\) associated with its in-plane SPhP resonance. Its highly tunable phonon modes and hyperbolic dispersion make hBN a promising candidate for applications such as control of thermal emission.
Azeotropic Volatility Behavior of Hydrous Ethanol Gasoline Mixtures

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In the United States, the ethanol blended in our fuels is anhydrous or 200 proof, which requires an additional energy intensive process to produce due to the binary azeotrope which is formed at proportions of 95.6/4.4 mass % ethanol/water at 1 atm. To avoid this added expense, there is interest to blend gasoline with hydrous ethanol mixed in these azeotropic proportions to be used as a renewable or partially renewable fuel. To evaluate the effect of the added water, a few studies have shown that improved efficiencies and pollutant reduction can be achieved when blending hydrous ethanol into our petroleum based fuels. In order to fully utilize the potential of hydrous ethanol blended fuels, research is needed to characterize these mixtures including the effects on relevant physical and combustion properties. Using an improved distillation method, the ongoing study explores the effect of blending hydrous ethanol with gasoline (in azeotropic proportions) on the volatility of the complex fluid. Results demonstrate a unique boiling behavior with the hydrous ethanol/gasoline mixtures. For samples consisting of 75–85 % hydrous ethanol by volume, the initial boiling temperatures were found to be nearly 10 °C lower than those of either ethanol or gasoline alone as a result of a complex azeotrope formed with the water, ethanol, and compounds found within the gasoline. The distilled fluid is sampled during the experiment, and the distillate compositions are determined using gas chromatography techniques. The composition has allowed for the identification of the azeotropic mixtures responsible for the reduction of boiling temperatures and the determination of the effect of hydrous ethanol on relevant thermo-chemical properties, including the enthalpy of combustion.
Radiative Properties of Periodic Micro/Nanostructures for Arbitrary Polarization

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Periodic nano/microstructures of varies shapes are commonly used in metamaterial design to manipulate light propagation. Due to the interference effect, the radiative properties (e.g., reflectance and transmittance) of an arbitrary linearly polarized wave cannot be fully described by the corresponding radiative properties of transverse electric and transverse magnetic waves. In this work, explicit mathematical relationship between the Fresnel’s coefficients and the reflectance (or transmittance) for a given polarization angle is derived for anisotropic metamaterials. A three-polarization-angle method is proposed to obtain the reflectance or transmittance for any polarization angle using the reflectance or transmittance of transverse electric (TE), transverse magnetic (TM), and another polarization status. The results are compared with rigorous electromagnetic wave simulations using the finite-difference time-domain (FDTD) method. Polarization-independent reflectance of metamaterials made of regular polygons is also demonstrated. The radiative properties obtained from the three-polarization-angle method are in agreement with those from the rigorous numerical simulation. This work may facilitate the investigation of eigen polarizations in metamaterials for polarization control.
Viscosity and Density of NaCl(aq), CaCl2(aq), MgCl2(aq) with dissolved CO2 at Temperatures from (274 to 449) K and at Pressures up to 100 MPa

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We report the viscosity and density of sodium chloride, calcium chloride and magnesium chloride aqueous solutions with and without dissolved CO2. The measurements were made in the single-phase compressed liquid region at temperatures between (274 and 449) K at pressures up to 100 MPa. The viscosity was measured with a vibrating-wire viscometer while the density was measured by means of a vibrating U-tube densimeter. The initial results with the vibrating-wire viscometer for NaCl solutions without dissolved CO2 were found to exhibit a systematic error that increased with the electrical conductivity of the brine and hence was worst at high temperatures and high salt concentrations. This issue has been addressed with a semi-empirical modification of the working equation for the vibrating-wire viscometer. Measurements of the viscosity and density in the brines under CO2 addition were made at salt molalities of up to 5 mol·kg\(^{-1}\) and are associated with relative uncertainties of 0.1 % for density and 2 % for viscosity. The results for both properties have been correlated as functions of temperature, pressure, salt molality and the mole fraction of dissolved CO2. For viscosity, we used a simple modification of the Vogel-Fulcher-Tamman equation while, for the densities, a modified Tammann-Tait equation, incorporating a correlation of the partial molar volume of dissolved CO2, was employed.
Confinement Effect on the Dynamics of Concentration Non-Equilibrium Fluctuations

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It is well-known that a macroscopic gradient affects fluctuations in a fluid by making them long-ranged and enhancing their amplitude [1]. The study of fluctuation dynamics reveals that small fluctuations exhibit diffusive lifetimes, while fluctuations larger than a characteristic size live shorter because of gravity, as theoretically [2,3] and experimentally [4] demonstrated. In this presentation we will report a combination of experimental, theoretical and numerical evidence of a dramatic slowing-down for fluctuations larger than a size dictated by the extent of the system parallel to the gradient [5]. Results from dynamic shadowgraph experiments [4] are complemented by theoretical calculations based on Fluctuating Hydrodynamics [1] and previously developed to investigate the intensity of fluctuations [6], as well as by numerical simulations [7,8]. The experimental data is found to be in excellent agreement with theory and simulations including realistic boundary conditions, demonstrating that the origin of the slowing-down is confinement.

References

Effect of Impurities on the Capture of CO₂ using Superbase Ionic Liquids

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Recently Ionic Liquids (ILs) composed of a tetra alkyl phosphonium cation paired with a superbasic anion have been reported to exhibit equimolar CO₂ absorption with efficient CO₂ capture and release. In particular these ILs show only small changes in viscosity after reaction with CO₂ unlike the amino acid based ILs which exhibit large increases in viscosity. In this work the effect of water on the CO₂ capture of [P₆₆₆₁₄][124Triz], [P₆₆₆₁₄][PhO], [P₆₆₆₁₄][Bentriz], [P₆₆₆₁₄][123Triz] and [P₆₆₆₁₄][Benzim] has been evaluated showing that depending on the anion, water can have a positive or negative influence on the CO₂ uptake. The effects of the presence or the absence of water on CO₂-IL interactions have been studied using ¹H and ¹³C NMR spectroscopy. CO₂ absorption/desorption cycles have also been carried out to evaluate the recyclability of the IL as well as studies on the viscosity of the IL before and after CO₂ absorption under dry and wet conditions. Various methods for CO₂ absorption have been used and compared as well as studying the effect of changing the cation. In addition to the effect of water, studies have also been carried out looking at the effect of other impurities commonly present in industrial gas streams eg. CH₄, H₂S, NOₓ and SOₓ.

References

Experimental Measurements and DFT of Adsorption of Methane, Water and Their Mixtures on Activated Carbons

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The physico-chemical phenomena occurring at interfaces, as for instance wetting, adsorption, and confinement effects, have a deep influence on the static and dynamic thermophysical properties of fluids confined in porous media. This work aims at studying the adsorption of pure methane, pure vapor water and their binary mixtures in porous confined media. From an experimental point of view, adsorption isotherms for pure components are measured on a magnetic suspension balance [1], coupled with a homemade steam generator that allows investigating P-T ranges above ambient conditions. For binary mixtures, an apparatus has been specifically developed based on a manometric technique [2] coupled with a compositional analysis system. From a theoretical approach, a Density Functional Theory that uses the SAFT-VR equation of state and weighted density approximations, was developed for non-associating and associating monomers in order to determine the adsorption behaviour of methane [3], water and their binary mixtures at pore scale. After a characterization of the sample through a correct determination of its pore size distribution, the experimental results are compared with modeled adsorption isotherms.
Measurement of Emissivity and Infrared Optical Properties at PTB

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The Physikalisch-Technische Bundesanstalt (PTB) operates in its department “Detector Radiometry and Radiation Thermometry” several facilities which allow the accurate measurement of the directional spectral emissivity, reflectivity and transmissivity. These facilities allow measurements of emissivity in air and under vacuum from 1.2 μm to 100 μm in a temperature range from -40 °C to 1000 °C and up to 2000 °C at 1064 nm. Reflectivity and transmissivity could be measured at room temperature up to wavelengths of 1000 µm. The accurate knowledge of the emissivity, reflectivity and transmissivity of a material is crucial for a variety of technological applications whenever heat transfer by radiation becomes significant or temperature is monitored via radiation thermometry. Recent examples of applications which require very low uncertainties of emissivity are absorbers for solar thermal electricity generation and coatings of onboard reference blackbodies for benchmark missions in space. Here we give a short overview of the capabilities for non-contact temperature measurement in the department. In more detail we present the facilities used for optical property measurements and give examples for recent results. The emissivity measurement setup under vacuum is part of the Reduced Background Calibration Facility (RBCF) at PTB where all critical components of the optical path are under vacuum and cooled with liquid nitrogen. Hereby the infrared background radiation is largely reduced. The facility under air is precisely temperature stabilized to provide a constant background. The scheme for direct emissivity measurements at both facilities is based on the measurement of the spectral radiance of a sample inside a temperature stabilized spherical enclosure with respect to the spectral radiance of two reference blackbodies at different temperatures whereby the remaining background is cancelled. Directional spectral emissivities above 1000 °C are measured with a dynamic method based on a modified laser flash apparatus for thermal diffusivity measurement.
In this contribution, the effects of electrolytes on the phase behaviour of carbon dioxide hydrate forming systems are presented. The phase behaviour of the simple carbon dioxide hydrate system, the mixed carbon dioxide - tetrahydrofuran (THF) hydrate system, and, finally, the effect on the phase behaviour of different overall concentrations of sodium chloride will be elucidated. In addition, the competing effects between THF and an electrolyte of the metal halide series and their impacts on the phase behaviour of the hydrate forming systems will be discussed. The strength of hydrate inhibition by metal halides is compared and, a quantitative analyses between the effect of anions and cations is made in order to gain some understanding on the mechanism of electrolyte inhibition on hydrate formation.
In the industry of dough and tortilla is important to characterize the color of the maize (Zea mays L.) grain, as it is one of the attributes that directly affect the quality of "tortilla" consumed by the population. For this reason, the availability of alternative techniques for assessing and improving the quality of grain is very welcome [1, 2]. Photoacoustic spectroscopy (PAS) has proven to be a useful tool to characterize maize grain. So, the objective of the present study was to determine the optical absorption coefficient $\beta$ of maize grain used to make "tortilla" from two regions of Mexico: a) "Montecillo Texcoco" productive cycle (2012-2013), b) "Sinaloa – Guasave" productive cycle (2013-2014). Traditional reflectance measurements, physical characteristics of the grain and nutrient content was also calculated. The experimental results show different behaviors for maize grains.

References

Photothermal Radiometry Characterization of Zinc Oxide Based Varistors Doped with Antimony Oxide

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Zinc oxide varistors are voltage-limiting ceramics devices with highly nonlinear resistance, used as overvoltage surge protection in electrical circuits. ZnO-based varistors are semiconducting ceramics fabricated by sintering of ZnO powders with small amounts of additives to enhance the non-linearity of the varistor’s behavior. The origin of their non-ohmic behavior lies in their microstructure, where ZnO grains are three-dimensionally separated from each other by grain boundary layers formed by the reactions of additives with each other and with ZnO. The electrical properties are so sensitive to the microstructure because the breakdown voltage is related to the grain size. The microstructure, electrical and thermal properties of ZnO based varistors both depend on type and content of dopant as well as the method of formulating ZnO and the processing condition [1-3]. In this work, photothermal radiometry is used to obtain the thermal diffusivity of ZnO and ZnSb2O6 performed by a traditional ceramic method and sol-gel method. Also the heat capacity and the thermal conductivity are determined. The correlation of the obtained thermal properties and the I-V response and nonlinear coefficient is investigated. The study is complemented by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

References

Thermal Conductivity and Diffusivity of Solid/Liquid Phase Change N-Alkanes Determined by the Transient Hot Wire Technique

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The transient multi-current hot wire technique is used to determine simultaneously the thermal conductivity ($\lambda$) and thermal diffusivity ($\alpha_T$) of the solid/liquid phase change linear $n$-alkanes at atmospheric pressure in the range 258-348 K. These compounds are used in Phase Change Materials (PCM) for energy storage and recovery. The same set-up was used to measure $\lambda$ and $\alpha_T$ of the liquid and the solid states at different electrical currents. Both odd- and even-numbered $n$-alkanes were considered ($n$-pentadecane, $C_{15}H_{32}$, $n$-hexadecane, $C_{16}H_{34}$, $n$-heptadecane, $C_{17}H_{36}$, $n$-octadecane, $C_{18}H_{38}$, $n$-nonadecane, $C_{19}H_{40}$, and $n$-eicosane, $C_{20}H_{42}$). The obtained results were compared with available literature data. In fact, no literature data were found for $\alpha_T$ of the $n$-alkanes considered in this study. The values obtained for the liquid phase cannot be in any reliable way extended to the solid phase. The discontinuity of $\lambda$ near $T_m$ was found to be higher for the $n$-alkane having the larger number of carbon atoms. The diffusivity $\alpha_T$ of $C_{16}$, $C_{18}$ and $C_{20}$ is larger in the solid phase than in the liquid phase. Low accuracy for both $\lambda$ and $\alpha_T$ were obtained near (and below) the solid/liquid phase transition of the studied $n$-alkanes, due to the latent heat of melting/crystallization that may affect the temperature of the wire.
Magnetorheological (MR) fluids are dispersions of, highly magnetizable, carbonyl iron powder in a non-magnetic carrier liquid. These are materials that in the absence of magnetic fields behave as conventional fluid. Nevertheless, in the presence of a magnetic field, those fluids can be transformed rapidly from a fluid-like state to a solid-like state, due to the preferential aggregation of the microparticles which lead to the formation of chain-like structures in the direction of the applied field. This is considered to be one of the most important characteristic of those smart fluids. The research about thermal properties of this kind of fluids shows that the thermal conductivity could be enhanced with the increment of microparticles concentration and applying an external magnetic field. However, MR fluids based on microparticles are subjected to challenges in practical applications due to the lack of versatility. In recent years several studies have been carried out to understand how additives such as carbon nanostructures change the materials properties. In this work we investigated MR fluids loaded with carbon nanofibers, which are nanostructures with a high thermal conductivity, with the goal of enhancing the thermal properties of conventional MR fluids. The versatile and accurate technique known as thermal wave resonator cavity technique was used to the measurement of the thermal diffusivity applying a uniform magnetic field. From these results, the thermal conductivity was studied in function of the carbon nanofibers/carbonyl iron microparticles and the applied magnetic field. The results show that using nanostructured materials as dispersal phases can improve the thermal MR performance.
To extract the thermal conductivity, thermal diffusivity and possibly volumetric heat capacity of micro- to nanoscale size fine fibers, the samples, which are undergoing either a constant or modulated Joule heating, are suspended between two heat sinks. Modeling of the heat transfer process through the samples is improved from the literature analyses by incorporating the heat loss contribution on the heated fibers. The magnitude of such influence is determined by a dimensionless parameter by which samples having low thermal conductivity and large aspect ratio receive significant impact. In addition to the modeling melioration, a series of measures are developed to improve the sample preparation, experimental operation and data reduction especially for the metal coated electrically non-conductive fibers. The developed models are validated by the thermophysical property measurements of platinum wires and glass fibers. With consistent calibration results to the literature values, the techniques are employed for the thermal property determination of natural and synthetic spider silks.
The thermal conductivity of $\{x\text{CH}_4 + (1-x)\text{C}_3\text{H}_8\}$ with $x = 0.949$ was measured at temperatures from (200 to 423) K and pressures between (10 to 31) MPa, using an transient hot-wire method. The measurements were conducted with a recently constructed transient hot-wire instrument. Two 12.5 μm diameter platinum wires of length 23 mm and 57 mm were arranged in opposite arms of a Wheatstone bridge in order to eliminate the end effects arising from axial conduction. These new data on transport properties of natural gas mixtures will assist to achieve more efficient designs of industrial processes and equipment. The data acquisition system (capable of multi-channel sampling at 1 MHz) interrogated several voltages in the circuit simultaneously. The pressure transducer and platinum resistance thermometer were calibrated before the measurement, and the resistances of the two platinum wires were determined as a function of temperature. Performance of the instrument was verified by measuring the thermal conductivity of nitrogen and helium over a range of temperatures and pressures. The results for the thermal conductivity of $\{x\text{CH}_4 + (1-x)\text{C}_3\text{H}_8\}$ with $x = 0.949$ are compared with the limited literature data [1, 2] and values predicted from the extended corresponding states model implemented in REFPROP 9.1 by plots of deviations from that model.

References

Design of the Guarded Hot Plate Apparatus for the Measurement of High-Temperature Thermal Transmission Properties

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A high-temperature guarded hot plate apparatus is designed for the measurement of thermal transmission properties up to 1000 °C. The guidelines ASTM C177 and ISO 8302 are thoroughly analyzed and followed as design principles. The maximum transfer factor of the specimen that can be measured with the designed apparatus is 5 W/(m · K). To conduct the thermal transmission measurement in various non-oxidizing atmospheres the apparatus is designed to be inside a high temperature chamber. The heating part of the apparatus is surrounded by three radiation shields that protect the body of the chamber. The heating part is vertically divided into three layers; lower cold plate, hot plate, and upper cold plate layers. Because the apparatus should accommodate two specimens with the thickness up to 100 mm and the installation of the specimens should be easy, the hot plate and upper cold plate layers are designed to be movable independently. Since the parts in the heating area is exposed to high temperature up to 1000 °C, high temperature resilience of the moving parts inside the chamber is main concern. The moving parts are designed so that the thickness of the specimens is defined by the vertical distance between the plates with fixed maximum pressure to the plate. Therefore, both compressible and incompressible specimens can be measured with the apparatus. The vacuum system is also installed for the initial evacuation of the chamber to remove moisture contained in the parts and specimens inside the chamber.
The effect of temperature on the dynamic viscosity of crude oils has been widely investigated. In particular the heating process, where it is well known that viscosity of crude oils decreases when increasing temperature. However, there is a lack of information of what happens counterclockwise, namely cooling process. The cooling process phenomenon is the most important in different stages of crude oil production and the study of rheological parameters is fundamental to improve strategies in extraction and transportation of crude oil. Crude oil suffers considerable drops of temperature when it is extracted, i.e using modern techniques in deep-water reserves. This decrease in temperature induces a more complex flow behavior of crude oils, which is necessary to investigate in order to ensure the correct and safe transportation of this material. Experimental data have shown that during the heating process at constant shear rate, the viscosities measured at any given temperature are higher than the ones measured during the cooling process. This effect may be explained by the structural changes occurring during the experiment. The ascending-descending curve presents a temperature hysteresis, which is more common in waxy oils. There is a critical temperature beyond which the viscosity is altered and it may depend on the composition of the oil. In this work we present the ascending-descending curve for some oils and the temperature hysteresis on viscosity.
Clathrate hydrates are crystalline inclusion compounds, where hydrogen-bonded water molecules (host molecules) encage guest molecules – such as methane and CO2. The interactions between the hydrate cages and the guest molecules are usually through weak van der Waals forces. Using electron spin resonance (ESR) spectroscopy, our group has measured the thermal stabilities of methyl radical induced with gamma-ray in pure CH4 and CH4+CO2 mixed hydrates. Gamma-radiation has enough energy to transfer electron from water or methane molecule to CO2 molecule. Considering the low stabilities of the species formed after electron transfer, their decomposition produces an additional reaction chain, generating stable radicals. To investigate the mechanism of methyl radical formation in mixed hydrate systems, the results on gamma-ray and UV irradiated CH4+CO2 mixed hydrates were compared. Additionally, the same experiments with mixed hydrates prepared with D2O only under gamma-ray irradiation were conducted. From the analysis of the gamma-ray-irradiated mixed hydrates prepared with D2O, a dominant synergistic mechanism in radical formation was suggested. Moreover, the results show different radical formation efficiencies dependent on the irradiation sources, which contributes to the mechanism suggested. The methyl radical has an important role in combustion chemistry, in atmospheric chemistry and in planetary science – such as an oxidant and reducing agent.
High-pressure, high-temperature properties of carbon dioxide/water solutions are of direct interest to geophysics and explosives modeling, and obtained results may inform models useful at lower pressures. Due to the many difficulties of working with these solutions, data to date are scarce; previously reported observations of phase behavior have been limited to pressures lower than 3 kbar. We report measurements of the phase behavior of this system, including fluid-fluid and fluid-solid equilibria, to pressures of 60 kbar and temperatures of 400°C.
Specific Heat of Vegetable Oils as a Function of Temperature Obtained by Adiabatic Scanning Calorimetry

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Vegetable oils can undergo changes in their properties when they are subjected to processes such as extraction, purification, cooking, frying or chemical modifications that are required depending on the application in the food industry [1]. One of the main thermal property of the vegetable edible oils is the specific heat, which allows us to evaluate the transformation undergone a sample to be stored for some time and varying temperature, which can be measured by a calorimetric technique [2]. By using an adiabatic scanning calorimeter (ASC), the specific heat of vegetable edible oils were obtained as a function of temperature, in the range of 35°C to 70°C, for four different vegetable edible oils (extra virgin olive oil, virgin avocado oil, grape seed oil and sesame oil), finding for specific heat of samples a linear behavior dependence when the temperature is increased.

References

There is a disagreement in the values of the standard state thermodynamic properties for ionization of water calculated from potentiometric [1] and calorimetric measurements [2] at temperatures above 473 K. Accurate standard state (infinite dilution) thermodynamic properties for the ionization of water at high temperatures and pressures are very important in the study of almost all ionic equilibria in aqueous solutions. Because of increasing non-ideality of the electrolytes in even dilute solutions [3], the extrapolated experimental thermodynamic values to standard state (infinite dilution) conditions become more uncertain as the temperature increases. Since ionization of water is perhaps the most important acid-base reaction, it was decided to reinvestigate this disagreement between potentiometric and calorimetric measurements. Using ionic additivity, values for the changes in the standard state Gibbs free energy, enthalpy, entropy, heat capacity, and molar volume for ionization of water, at steam saturated pressure up to the temperature of 573.15 K, are calculated from the recently available corresponding values for the standard state partial molar properties of HCl(aq) [4], NaCl(aq) [5], and NaOH(aq) [6, 7]. Comparison of the present study with the literature data indicate that in fact there are no disagreements between the above mentioned standard state thermodynamic properties for ionization of water calculated from potentiometric and calorimetric measurements. The apparent disagreement is, however, the result of the model chosen to represent the potentiometric data.

References:

Comparative Optical Characterization of Edible Vegetable Oils by Using Photothermal Techniques

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The optical characterization of edible oils is important, among other reasons, because has been applied to monitor the deterioration due to the humidity and thermal stress of this kind of oils [1]. In the present study the optical absorption spectra of several vegetable oils such as avocado, sesame, olive and grape seed oils were obtained by using two different photothermal techniques, photopyroelectric spectroscopy (PPES) [2] and photoacoustic spectroscopy (PAS) [3]. PPES and PAS were used to obtain, separately, the optical transmission spectra of the oil samples. By using the obtained transmission spectra, and neglecting the sample reflectivity, it was obtained the sample optical absorption spectra from both techniques. Also the optical absorption spectra of the oil samples were obtained by photoacoustic spectroscopy. By comparing both absorption spectra, obtained by transmission configuration of PAS and PPES, and the absorption spectra obtained by PAS, it was observed than both spectra are lightly affected by the reflectivity of the samples but they have the same optical absorption bands.

References

We present a simple method to measure absorption loss in thin film dielectrics. The absorption characterization method is a photothermal technique based on thermal lensing. The method measures the defocusing of an incident probe beam caused by a thermal lens generated by absorption of the incident pump beam. The specific application is for thin films deposited on fused silica substrates. The concept of the method is simple. The pump beam is selected specifically to match the wavelength at which one desires to know the absorption. In the case of a thin film on a substrate, the absorption in the thin film acts as a heat source that causes a temperature increase of the substrate. Since the refractive index of the substrate changes with temperature this acts as a lens focusing a probe beam of shorter wavelength that passes through the whole thickness of the substrate. Thus the final focus of the probe beam is altered by the absorption of the sample. Quantifying the change in the focal plane of the probe beam allows the determination of the sample absorption. This is done using a four-quadrant detector and cylindrical lenses to generate a focus error signal. The technique has a sensitivity of less than 10 ppm absorption @1064nm wavelength. Sensitivity is limited by the bulk absorption of the substrate. Excellent results were obtained with both amplitude modulated and pulsed pump laser beams. One of the main advantages of the technique is that the pump beam does not need to be tightly focused on the sample and the detection scheme can be placed far away from the sample (a collimated probe beam is used).
Accurate measurement of the thermophysical properties of new, exotic carbon composites is critical in their design process. Researchers are targeting a carbon-based material with a rising thermal conductivity when subjected to increasing temperatures, with an extremely low thermal expansion coefficient through this temperature range. Through the initial Research & Development stage, fast and accurate measurement of these parameters helps to delineate different approaches to achieving the desired materials mechanical and thermal properties. The use of the modified transient plane source (MTPS) method provides for a powerful and quick way to determine the thermal conductivity in complex carbon composite materials. Thermal expansion is measured with a high-resolution interferometer. The accuracy of both methods is verified in testing certified reference materials. Ranking of a variety of carbon composite samples through a range of temperatures is presented. Thermal conductivity is measured over a temperature range of 25 to 200°C, and thermal expansion from room temperature to 1000°C.
Dynamic Data Evaluation Evolution for the Metallic Systems

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The concept of dynamic data evaluation has been employed in the Thermodynamics Research Center (TRC) at within NIST to develop a database of critically evaluated thermodynamic property data for the organic, predominantly liquid and gaseous, phase systems. NIST additionally develops the tools used for data collection and analysis, both prior to addition to the database as well as data curation. The vigilant maintenance of the data quality in the SOURCE database has proven to many industrial sponsors the value of a dynamically evaluated database. An expansion of the focus of TRC into the fields of metallurgical systems began in early 2013 as a part of the Materials Genome Initiative, a multi-agency effort designed to create a materials innovation infrastructure that includes: computational and experimental tools, digital data and collaborative networks in the materials community. It is the goal of the TRC to provide dynamic, modern, thermodynamic data—however this requires the development of a both a data structure and that ability to communicate between different platforms. The first effort for TRC was to develop both a data structure and software for data capture. Differences arise in the structure due to the presence of multiple phases in the solid state, compared to TRC’s traditional organic system consisting of phases that are classified as condensed liquids. The presentation will discuss the challenges in metallurgical thermodynamic data and developed solutions that allow TRC to capture the data.
To understand the crystallization phenomena better, this work aims to investigate the crystal growth from an aqueous solution on a cooled surface theoretically and experimentally in terms of irreversible thermodynamics aspect for (i) estimating the magnitude of the temperature jump at the crystal-liquid interface, (ii) quantifying the effect of the coupling of heat and mass transport and (iii) showing the error one may do assuming that all of the heat of crystallization is transferred into the cold side (i.e. to the crystal side) and the temperature values of both sides (crystal side and the liquid side) of the interface are equal during phase transition. Ice formation from pure water is taken as an example case. A high-quality quartz growth cell was designed and constructed for this crystallization experiment. The cell underneath surface was cooled via a heat exchanger. Data was collected during crystallization on the heat exchanger surface. Thermochromatic Liquid Crystal was used to detect the temperature profile at a micro scale both in the solution and under the ice crystals. To define the fluxes and forces of the system, the excess entropy production rate for heat and mass transport into, out of and across the interface (between ice surface and liquid) was used. The method describes the interface as a separate, two-dimensional phase in local equilibrium. Coupled heat and mass flux equations from non-equilibrium thermodynamics were defined for crystal growth and solved taking the advantage of the Onsager equations. A temperature jump at the ice-water interface was detected up to 1.7 °C. This observation is the experimental proof for the existence of an interfacial temperature jump during liquid-solid phase transition. Coupling coefficients and all transfer resistivities at the interface of a growing ice on a cooled surface was also defined. Based on this knowledge, it is possible to improve film or fugacity models for the interface, change current modelling of phase transitions and eventually help the prevention of crystal growth at unwanted locations (such as scale layer formation on heat exchanger surfaces) in process industry saving considerable capital and operational costs.
Calorimetry and especially High Pressure Differential Scanning Calorimetry (HP-DSC) was found to be a relevant tool for investigating the thermodynamics of formation and dissociation of gas hydrates as it is able to simulate the temperature and pressure conditions of their formation. Originally applied to fields related to oil and gas production and flow assurance [1], then extended to the study of oil-water-gas systems and the emulsion stability of oils with hydrate [2], it has now been involved in several new studies. Indeed, carbon dioxide sequestration by CO$_2$/CH$_4$ exchange in natural gas hydrates present in marine sediments, carbon dioxide hydrates reversible formation/dissociation for refrigeration loops, hydrogen storage system through the formation of hydrogen hydrates [3], and many other studies involve the use of HP-DSC. However, the technique still has some limitations which are linked to the fact that the gas hydrate formation in the calorimetric cell occurs at the gas-liquids interface. It leads to problems such as inefficient gas dissolution, long induction times, formation of a hydrate crust covering the gas/liquid interface, low hydrate to water conversion, etc. Thus it makes for example difficult or impossible the accurate determination of heat capacities or of kinetics of formation/dissociation. The presented work will cover these new fields of application of the technique and will include the description of a new high pressure, mechanically stirred calorimetric cell which overcomes the existing limitations. This cell has been developed by the Laboratory of Complex Fluids and their Reservoirs of the University of Pau and Pays de l’Adour (patent FR 2993980) and has been industrialized and commercialized by SETARAM Instrumentation.

References

Some of the environmental problems are caused by gaseous emissions from thermal processes, mainly by the burning of fossil fuels. Several alternatives to reduce such emissions have been discussed worldwide and the use of biofuels is a promising one. This study provides information of five lignocellulosic materials, namely pine sawdust, sugarcane bagasse, coffee and rice husks, and tucumã seeds to be used as biofuels in thermochemical processes. Particular attention is devoted to the residues and gaseous emissions (CO, CO$_2$, SO$_2$ and NO) generated by the biomasses combustion process in a Drop Tube Furnace (DTF). The DTF is a laboratorial reactor scale that consists of an electrically heated vertical silica tube of 400 mm length and 60 mm inner diameter. Combustion experiments were performed in triplicate for each sample and the gaseous emissions were continuously measured by a set of gases analyzer. A 1.5 L min$^{-1}$ air upflow rate and 0.3 g min$^{-1}$ mass flow were applied and the temperature was maintained at 1000°C. Thermogravimetry (TGA), Scanning Electron Microscopy (SEM images) and Energy Dispersive Spectroscopy (EDS analysis) were used for the physical-chemical characterization of both in natura biomasses and the residues generated from the combustion. The results show that CO$_2$ emissions ranged between 11 and 14 mg Nm$^{-3}$ g$^{-1}$. Sugarcane bagasse showed the lowest limits of SO$_2$ and NO emissions (31 and 11 mg Nm$^{-3}$ g$^{-1}$, respectively) and tucumã seeds provided the lowest values of CO emissions (2540 mg Nm$^{-3}$ g$^{-1}$). TG/DTG curves of the solid residues aided in diagnosing the performance of the DTF combustion experiments. According to the results, the organic matter present in the residues varied from 4 to 72%, which shows the efficiency of the combustion process widely varies in function of the type of biomass used. The chemical composition of the residues showed different proportions of inorganic elements (Si, K, Na, S, Cl, P, Ca, Mg, Cu, Zn and Fe) are present in the residues, which also demonstrates that individual behavior is a consequence of the diversity of the biomass properties. The knowledge of some leading trends is important for the understanding that generalizations of processes cannot be applied when different biomasses are used.
Surface Tension Calculation of molten salts ReCl₃-ACl (Re=Y, La, Ce, Pr; A=Na, K)

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The electrolysis of molten salts containing rare earth chlorides has been widely used for production of rare earth metals and their alloys. Information about the surface tension of molten salts is essential for understanding the structure of the systems and for upgrading the technology of the electrolytic production of rare earth metals. In this paper, the method for calculating the surface tension of molten salts containing rare earth chlorides based on Butler’s original treatment was described. A new approach to estimating the partial excess Gibbs energy in the surface phase of molten salts using thermodynamic data obtained from the CALPHAD (calculation of phase diagram) technology in the bulk phase was proposed in order to improve the accuracy and applicability of the above method for surface tension calculation. Model parameters are dependent on temperature and composition of molten salts in our treatment, which are supposed to be more reasonable in contrast to earlier work. As examples for illustration, surface tensions of molten salts ReCl₃-ACl (Re=Y, La, Ce, Pr; A=Na, K) were calculated using the method proposed in the present work. The calculations of surface tension of LaCl₃-ACl (A=Na, K) systems from our method agree better with the experimental data than those from the method in previous work. It’s believed that our method has better applicability for predicting the surface tensions of various molten salts containing rare earth halides.
When simulating refrigeration systems or equipment, knowledge of refrigerant thermodynamic properties is required. While some of the refrigerants are made of pure fluids, some of this refrigerants are made by mixing of two or more pure refrigerants with a predetermined percentages. In modern trade and science, it is compulsory to get the same results in everywhere for the same inputs or measurements. Properties of refrigerants are a major part of international trade, therefore, it is a subject of interest of international standards. International Standard Organization (ISO) was prepared a standard for calculating real gas equation of states, for pure fluids and mixtures. The standard name is ISO 17584:2005(E). In the standard, Equations of States were given in Helmholtz free energy form. In this study a computer model was developed based on ISO 17584 equation of state and cubic spline curve fitting models developed by using saturation thermophysical properties of the refrigerants and refrigerant mixtures. Java programming language was used to model equation of state. As an example the equations for R1234yf and R410A were presented in this paper. With the new model, thermodynamic properties of R1234yf and R410A were compared with REFPROP 9.0. It shows that the total mean deviations of the new model are less than 0.5%.
Effects of Hydrogen Bonding, Viscosity, and Polarity on Heat Transfer Nanofluids Containing Fe₂O₃ Nanoparticles

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the
High-Pressure and Temperature Viscosity Standards in the Range Required for Heavy Oils

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The main purpose of this work is the design, validation and implementation of an experimental system operating in a range of temperature that goes from ambient to reservoir conditions (~120°C) and up to 1000 bar of pressure to measure the viscosity of reference/calibration fluids with good accuracy – aimed to better than 2% at high-pressure (HP) conditions. For this purpose, the design of a hydraulic system is proposed and implemented; this system was designed to allow simultaneous measurements of viscosity and density of a sample. The viscosity measurement system includes different laboratory equipment: a HP syringe pump, a transfer fluid piston cylinder, a high-pressure falling body viscometer equipped with a variety of geometries that allow for the determination of viscosities covering five orders of magnitude, a thermal bath, an oscillating U-tube densitometer and a high-accuracy Stabinger viscometer. The experimental setting is validated against pure reference fluids, including water, obtaining average deviations better than 0.5% at high pressure. Further HP estimations of other relevant fluids, such as hexadecane, are also determined. Once the experimental system has been validated, three Newtonian viscosity reference blends of 1000 mPa·s, 10000 mPa·s and 50000 mPa·s have been studied and their reference tables extended from atmospheric pressure to 1000 bar in a temperature range of 20-120 °C. This has resulted in the development of calibration tables covering a viscosity range of $10^2$-$10^6$ mPa·s with accuracy better than 4% at high viscosity conditions in normal scale. In a logarithmic scale the uncertainty is better than 0.5% for the full viscosity range. Afterwards, representative, light to heavy, Mexican crude oils have been measured and several comparative results are presented.
We measured isobaric heat capacities of liquid R245fa with high reliability. Our group constructed a flow-calorimeter in 1996 for measuring specific heat-capacity at constant pressure of HFC liquid refrigerants. In 2014, Tanaka and Fujiwara reconstructed the apparatus of a flow calorimetry with an improvement for achieving a stable mass-flow-rate by introducing plastic accumulators and parallel needle valves. We confirmed that the apparatus is able to measure isobaric heat-capacities with unmeasurable level heat loss and repeatability within the uncertainty under simple operation. Isobaric-heat-capacity measurement was applied to liquid R245fa. The measurements were obtained at multiple points of state parameters, a pressure of 500 kPa in a temperature range from 280 K to 325 K. The expanded uncertainty (coverage factor of $k = 2$) for heat capacity is predicted to be from 0.40 % to 1.00 %.
Selective and Dynamic Control of Optical and Radiative Properties with Film-Coupled Metamaterials: Numerical Modeling and Temperature-Dependent Spectrometric Characterization

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Selective control of thermal radiation has numerous applications in energy harvesting, thermal management, and microelectronics. Past work has demonstrated that surface radiative properties can be successfully tailored with multilayer structures and micro/nanostructures. However, temperature-dependent radiative properties are little studied, which are crucial for applications at elevated temperatures. Besides, reported radiative properties are mostly static, while active tuning of surface emission or absorption is greatly beneficial to radiative thermal control. We will present our recent progresses in both numerical design and spectrometric characterization of film-coupled metamaterials with an emphasis on temperature-dependent optical and radiative properties. With finite-difference time-domain method, a metamaterial solar absorber with strong spectrally-selective absorption/emission has been designed. Optical and thermal radiative properties of fabricated samples will be characterized in a broad spectral regime from UV to mid-IR regime under different temperatures. An FTIR spectrometer along with a variable-angle reflectance accessory is used to indirectly measure the room-temperature absorptance/emittance spectrum. A novel FTIR fiber optics method along with a home-built heater assembly is developed to measure the temperature-dependent optical reflectance from room temperature up to 400degC. Along with a blackbody source and external optics, the spectral-directional emittance of the sample will be directly measured at higher temperatures up to 1000degC. Thermal stability and temperature effect on the optical and radiative properties will be experimentally studied, which is crucial particularly for the practical high-temperature applications such as concentrated solar power with these advanced materials. On the other hand, we have designed a switchable film-coupled metamaterial with a spacer layer made of VO2, which experiences metal-insulator transition at 68degC. Upon the VO2 phase change, magnetic resonance could be either turned on or off, resulting in a switchable spectrally-selective emission peak in the mid-infrared. With a temperature-controlled heating stage inside the reflectance accessory, we will measure the infrared emittance of a fabricated switchable metamaterial sample at temperatures below and above its phase transition point, thereby experimentally demonstrating the dynamic control of thermal emission with a thermally induced mechanism. Such a “smart” coating material could find applications in radiative cooling for buildings and spacecraft systems.
We have developed the measurement technique of thermal contact resistance at bump joints in a flip chip assembly structure using the photothermal reflectance method. When the sample is heated by a modulated laser diode with the wavelength of 405 nm, the periodic temperature variation caused by heating is generated inside the Au bump. A continuous He-Ne laser with the wavelength of 633 nm is focused on the center of the bump of 30 μm in diameter to monitor the changes in the light reflection from the bump surface. We detect the reflected He-Ne laser from the bump surface by a balanced detector, and this reflected beam is proportional to the small temperature amplitude. Under these conditions, there is a phase lag between the reflected beam and the modulated beam, and this lag contains information about the thermal contact resistance. Therefore, it is possible to extract the thermal contact resistance by a curve-fitting analysis of phase lag data which is detected by a lock-in amplifier in the frequency domain. We changed the wavelength of the probe beam from 633 nm to 532 nm due to the larger temperature dependence of Au reflectivity. By using the apparatus, we conducted a high temperature storage test at 250 °C and measured the thermal contact resistance and the electrical resistance. In this measurement, we have succeeded in detecting the thermal contact resistance change caused by deterioration. During the deterioration test for 60 hours, the electrical resistance increased about 6 times at a maximum and the thermal contact resistance about 13 times at a maximum.
Pillar array surface structures fabricated with ZnO:Ga (GZO) and ZnO:Al (AZO) were proposed as the emitter for near-field thermophotovoltaic (TPV) systems. 2D square pillar array surface structures with critical sizes of hundred nanometer are able to manipulate near-field radiative transfer spectrum in the near-infrared range. Doped ZnO is used as the emitter material due to the resistance to high temperature and changeable optical properties by changing the doping ratio. The spectral control ability of doped ZnO pillar arrays was studied by the finite-difference time domain (FDTD) method, where the emission of thermal radiation was directly simulated using the Langevin approach to characterize the thermal fluctuations inside the high temperature emitter. The permittivity of AZO and GZO was fitted with Drude-Lorentz model from experimental data and taken into the FDTD simulation with piecewise linear recursive convolution (PLRC) algorithm. The spectral radiative flux was calculated between two doped ZnO pillar array surfaces and also from the doped ZnO emitter to the GaSb cell surface to explain the influence of pillar array size parameters and ZnO doping ratio on the radiative flux spectrum. In consideration for TPV output power, the heat flux in the GaSb bandgap spectrum is discussed with comparison between ZnO pillar array emitters and traditional metallic emitters.
Thermal-Diffusivity and Heat-Capacity Measurements of Sandstone at High Temperatures Using Laser-Flash and DSC Methods

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The well known contact-free, laser-flash method was used for measurement of the thermal diffusivity (a) of natural sandstone samples. The experimental procedure was conducted using the micro-flash apparatus (LFA 457). The measurements have been made over the temperature range from (302.9 to 774.3) K. The isobaric heat capacities (Cp) of the same sample were measured over the temperature range from (308 to 763) K using DSC 204 F1. Uncertainties are 3 % and 1 % for a and Cp, respectively. Measured values of a and Cp together with density data were used to calculate the thermal conductivity (λ) of sandstone. Theoretically-based correlations for the thermal diffusivity (damped harmonic oscillator, DHO) and heat capacity (Debye and Einstein theories) were adopted to accurately represent the measured data. Correlation equations for the thermal diffusivity and heat capacity have been developed using the well-known theoretical asymptotic behavior of a(T) and Cp(T) for various temperature ranges (low- and high-temperature limits). The microscopic nature of the effect of temperature on a(T) and λ(T) behavior of sandstone will be discussed. Detailed interpretation and testing of the measured property data for sandstone using various existing theoretical and empirical models, in order to check their accuracy, predictive capability, and applicability, will be provided.
The state-of-the-art in calculating the thermodynamic properties of mixtures is based on the use of Helmholtz-energy-explicit equations of state for each of the components of the mixture and an excess term that accounts for the non-ideality of the mixture. The excess part requires a few pair-specific fitted parameters. Mixing model parameters are available for a number of binary mixtures, but there are many binary pairs for which little or no experimental thermodynamic data are available. Ultimately we will arrive at a correlation that allows for straightforward predictions of the mixture parameters for an arbitrary mixture of fluids based on information about the molecular structure of each of the fluids (from the Quantitative Structure-Property Relationships (QSPR) framework) forming the binary pair. The first step is to apply the state-of-the-art mixture parameter fitting routines in order to obtain predictions of the binary pair parameters for all the current binary pairs that are included in REFPROP. After the binary pair interaction parameters have been obtained, a correlation will be developed for each of the binary pair interaction parameters as a function of QSPR fluid data. The successful application of this technique will allow the prediction of thermodynamic properties, including vapor-liquid equilibria, critical points, densities, and many other parameters of technical interest for binary pairs of components for which high-accuracy equations of state are available, but where no binary mixing model parameters exist.
A Helmholtz-energy-explicit Equation of State for 2-propanol (isopropanol)

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We present here a new high accuracy Helmholtz-energy-explicit equation of state for the thermodynamic properties of 2-propanol (isopropanol). This equation of state is valid from the triple point temperature of 185 K to 700 K and pressures up to 1000 MPa. In total, more than 2000 experimental data points were used in the construction of this equation of state. To resolve differences in the literature data, a limited number of high-accuracy \( p - \rho - T \) data were measured on high-purity 2-propanol in the liquid phase from \( T = (215 \text{ to } 420) \text{ K} \) with pressures up to 27 MPa using a two-sinker, magnetic-suspension densimeter. A total of 321 \( p - \rho - T \) data at 79 \( (T, p) \) state points were measured. The uncertainties expected for this equation of state are 0.1% in density, 5% in constant pressure specific heat, 1% in speed of sound, and 0.2 to 0.5% in vapor pressure.
Magnetorheological (MR) materials have the characteristic that their physical properties can be changed applying an external magnetic field. This is possible because they are formed by a non-magnetizable matrix in which micrometric particles are immersed. The magnetic field induces ordering of the microparticles, generating changes in the physical properties. The most of the studies have been focused on the effects of the magnetic field on the mechanical properties; however the effect of the aligning on the thermal properties as well as the relationship of the thermal transport and viscosity has not been fully understood. In this work, two types of magnetic fluids were studied using carbonyl iron particles in two matrices: silicone oil and silicone rubber. Thermal diffusivity and thermal conductivity of these magnetic fluids are determined using the thermal wave resonant cavity when the fluid is subjected to uniform magnetic fields at different intensities. The dynamic viscosity was also measured and the relationship with the concentration of the particles and the magnetic field strength was investigated. The results show that when the content of carbonyl iron particles is increased in the material, the thermal conductivity and thermal diffusivity are incremented and when the magnetic field intensity increases the thermal conductivity and thermal diffusivity increases even more. A functional dependence of the thermal conductivity and dynamic viscosity was found. Additionally we have shown that using high viscosity materials, the order induced in the microparticles can be kept for a long time and therefore the increase in thermal conductivity can also be maintained.
The current methods for treating cancer are radiation and chemotherapy, which could be complemented by methods for controlled release of drugs in order to reduce side effects. The advantage of the hyperthermia treatment is that the amount of drugs used is lower; its elimination from the body is faster and more economical than chemotherapy. Hyperthermia, also known as thermotherapy is based on heating of nanoparticles by the application of an alternating magnetic field. The increase of the temperature depends on the nature and size of the particles, the carrying fluid, the frequency and size of the applied magnetic field. The heating curves of the sample allow determining the quantity which provides the quantification of a given treatment known as specific absorption rate (SAR). In spite of the studies to analyze the diverse influence heating phenomena during hyperthermia treatments, several basic mechanisms responsible of the heating are not well understood. In particular those related to the structural ordering of the nanoparticles require additional investigation. It is known that magnetic particles can be aligned in a fluid using a constant magnetic field. This alignment can be a determining factor in modifying the thermotherapy effects in a given ferrofluid [1]. In this work, the role of a the alignment of the nanoparticles of a ferrofluid using a constant magnetic field superposed with the usually applied high frequency AC magnetic field is studied in ferrofluids made of 10nm iron nanoparticles in two types of fluids, kerosene and agar and allow us to find their respective SAR.

References

This research reports the feasibility study of novel interference excitation method for the point-of-care testing (POCT) device using micro optical diffusion sensor (MODS). The diffusion coefficient is an important parameter for the analysis of the conformation changes of the biological samples such as protein. Miniaturized one-chip sensing device which achieves a high-speed and high-sensitivity measurement of the diffusion coefficient would be applied to medical, drug development and biochemical field. In order to gain the signal-to-noise ratio drastically and detect the diffusion phenomena optically, it is important to create the high-contrast lattice-shaped concentration distribution of the small biological sample that experiences weak dielectrophoretic (DEP) force. We have newly proposed a fringe spacing control technique so as to concentrate the sample. By narrowing the fringe pattern of excitation laser in micrometer order continuously, the small sample is trapped and concentrated by dielectrophoretic force, and thick concentration distribution is induced. Consequently, we can gain a sufficient diffraction efficiency of the concentration grating. In this study, the preliminary measurement for the concentration method has been conducted. We have newly built a bench top apparatus which can change the width of interference fringes in micrometer order at the same sample area. The apparatus is composed of the mirror mounted on the automatic x-axis stage which controls the optical path and the lens which can control incidence angle of the excitation laser. The signal intensity excited by the concentration technique was successfully improved because the thick concentration distribution was generated. As a result, the validity of our proposed interference excitation method has been experimentally confirmed.
We propose an extension of Onsager’s theory, originally formulated to describe non-equilibrium aged systems, in order to analyze the dynamics systems characterized by degrees of freedom that relax in different time scales (aging). Our theory is based on the assumption of local quasi-equilibrium states in phase space having a non-stationary probability density. This assumption entails the existence of a time-dependent temperature of the system $T(t)$ reflecting lack of thermal equilibrium between system and bath, which enables us to formulate a Gibbs equation. The relation between the local quasi-equilibrium and bath temperatures is given in terms of a scale function. We show that the fluctuation-dissipation relation remains valid in terms of the local quasi-equilibrium temperature $T(t)$ of the system whose value depends on the timescale considered. The formalism is applied to systems with a slow relaxation dynamics and to granular systems.
Heat of Solution and Solvation of Water and Alcohols in ILs

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In this work the heat of solution at infinite dilution of water, 1-propanol, 1-butanol and 1-pentanol in ionic liquids was measured by Isothermal Titration Calorimetry (ITC). The alkyl chain length effect was explored in the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonylimide ionic liquid series and the cation effect was evaluated by comparison of the solvation in the butyl cation derivatives, butylimidazolium butilpirrolidinium, butilpyridinium and butilpiperidinium. Water and the alcohol series were used as molecular probes to elucidate the differentiation and magnitude of interaction of the –OH groups with the ILs. The trend of the heats of solvation along the alkyl chain length, as well as, the change of the molecular character will be presented and analysed to give insights into the structuration and nanostructuration of the ILs. Analyses of the results obtained by varying both the alcohol’s and the IL’s length allowed us to assess the trend shift in $\Delta H_{sol}$ and in $\Delta H_{solv}$ values, and thus on solution interactions along this ILs series, reflecting the discrimination between the polar and non-polar regions of the ILs. It was thus possible to highlight and experimentally support the existence of a Critical Molecular Size (CMS) limit for the nanostructuration, starting at $[C6C1im][NTf2]$, reflecting a change in the molecular structure of the liquid. A very small differentiation of the solvation was found by changing the cation, supporting the model that the solvation of the alcohols involves the interaction of the –OH group with the anion.

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A hot plate for guarded hot plate apparatus for high temperature measurement of steady-state thermal transmission properties are designed and fabricated. For the aim of the thermal measurements up to 1000 °C, tungsten is chosen as hot plate material because its stability at high temperature and small thermal expansion. The hot plate is to measure specimens of square shape with 300 mm × 300 mm dimension located on the both sides of the plate. The measuring area is 150 mm × 150 mm, around which an air gap of 2 mm width separates the hot plate from the guard plate. Inconel-sheathed heaters of 2.3 mm outer diameter are installed in the grooves patterned on the plates, and used to control and to quantify the thermal energy across the specimens. The heaters are sandwiched between the two tungsten plates that are bolted together. The design parameter is adjusted so that the temperature uniformity on the hot plate is within 0.01 °C and on the guard plate within 0.05 °C. A finite element analysis method is employed to design optimal heater patterns for the uniform temperature distribution of the hot plate, guard plate and cold plates. The temperature uniformity on the both sides of specimens and gap imbalance across the hot and guard plates are measured by 16 type N thermocouples with 2 mm diameter installed on the plates.
Ultrasound is widely used for imaging, measurement and diagnostics in the MHz region and is very familiar as a powerful medical diagnostic tool but also finds widespread application in engineering as a non-destructive testing tool. Typically ultrasonic wavelengths are in the mm-micron range, many times longer than the wavelength of visible light which limits the resolution that these systems can achieve. By using acoustic waves in the GHz region, it is possible to perform ultrasonic imaging and measurement using ultrasound with wavelengths less than that of visible light and, potentially, to achieve higher resolution than optical microscopy. However, as the frequency of the ultrasound goes up the attenuation rises steeply and it becomes a considerable technical challenge to generate and detect the acoustic wave with sufficiently signal-to-noise ratio to permit measurement and imaging. Despite this nanoscale ultrasonics has much to offer as a powerful diagnostic tool. In this paper we discuss some of the practical problems standing in the way of nano-ultrasonics and some of the solutions, especially the use of picosecond laser ultrasonics and development of nano-ultrasonic transducers[1] using layered and nanoparticle structures. We present experimental results showing the measurement of protein adhesion and imaging on cell phantoms and 3T3 fibroblast cells.

References

Towards TOTM As an Industrial Reference Fluid for Viscosity at High Temperatures and High Pressures

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Tris(2-ethylhexyl) trimellitate(TOTM) was recently suggested as an industrial reference fluid for high viscosity at elevated temperature and pressure. Viscosity [1] and density [2] data have been published covering the temperature range (303 to 373) K and at pressures up to about 65 MPa. The viscosity covered a range from about (9 to 460) mPa.s. In the present communication we examine several other aspects of the choice of TOTM that must be satisfied if it were to be adopted as an industrial standard. First, we present values for the viscosity obtained with a different sample of TOTM, for comparison with the previous data, to examine consistency among different samples. Furthermore, we report a study of the effect of water contamination on the viscosity of TOTM. Finally, in order to support the use of TOTM as a reference liquid for the calibration of capillary viscometers, values of its surface tension, obtained by the pendant drop method are also provided.

References

Experimental Measurements of Dissociation Conditions for Water + CO$_2$ + Decane Mixture in the Hydrate Formation

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Gas hydrates are crystalline ice-like inclusion compounds in which the guest molecules are trapped in lattices composed of cages formed by hydrogen-bonded host molecules under certain temperature and pressure conditions. In the past, gas hydrate formation has been regarded as a serious impediment to oil and gas production because the hydrate formation during production induces pipeline plugging; hence, extensive research has been conducted to avoid this problem. However, the utilization of gas hydrates has recently attracted great attention in various fields: natural gas transportation/storage, carbon dioxide (CO$_2$) capture and desalination. Hence, hydrate-based gas separation could be an alternative approach for CO$_2$ capture and further research and developments need to be performed for the industrial implementation. In this work, new equilibrium data (pressure, temperature and composition) for carbon dioxide (CO$_2$) + water (H$_2$O) + decane (C$_{10}$H$_{22}$) mixture have been experimentally measured to determine the stability regions and dissociation conditions of the formed hydrates. The hydrates have been formed in aqueous solutions with mass fractions (C$_{10}$H$_{22}$) of 0.05 and 0.10. The hydrates dissociation conditions have been measured using a modified apparatus designed and built to operate at pressures up to 35 MPa and temperature between (253 and 303) K based in the isochoric method. The expanded combined uncertainties of the dissociation conditions were evaluated to be 0.004 MPa, 0.015 K and 0.00025 %mol in pressure, temperature and composition, respectively. On the other hand, in the international literature there are no experimental data on the equilibrium mixture under study, reinforcing the importance of expanding the thermophysical experimental data of liquid hydrocarbon mixtures for a better understanding of the hydrate behavior.
Experimental Densities of the Thiophene + Octane and Thiophene + Decane Mixtures up to 353 K and 20 MPa

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The thermodynamic properties obtained experimentally are the basis for obtaining models semi-empirical used to represent and predict the behavior of fluids. The volumetric properties are important in the chemical industry, are used for the design, simulation and optimization of processes such as distillation, liquid-liquid extraction separation, among others. In addition, knowledge of the density data is the basis for the determination of other properties such as solubility and dynamic viscosity. In this work, experimental densities of two binary mixtures: thiophene (1) + octane (2) and thiophene (1) + decane (3) in the range of 313 to 353 K and up to 20 MPa are reported. The two mixtures densities were measured at five different compositions between x= 0 and 1. The measurement system was based on a vibrating tube densimeter (VTD) with a coupled data acquisition system. The densities of nitrogen and water were taken as calibration fluids for the calibration of vibrating tube densimeter. The total uncertainties of the densities measurements were estimated to be less than 0.04%. 

Latent Thermal Energy Storage (LTES) systems in buildings and buildings envelopes have received serious attention for reducing energy use in building sector. Here, PCMs (Phase Change Materials) that absorb or release the energy equivalent to their latent heat when the temperature of the material undergoes or overpasses the phase change temperature can be effectively applied. The application of PCMs in thermal energy storage has been well known in many fields, such as in solar energy storage, waste heat recovery, and smart air conditioning in buildings. However, PCMs can be incorporated in wallboards, concrete, plaster, roof, underfloor and insulation of buildings in dependence on their properties, encapsulation etc. The effectiveness and usability of particular PCM material for specific part of building envelope must be experimentally verified case by case, in order to develop material having optimal thermophysical properties that allow moderation of interior climate temperature on desired value in dependence on changes of exterior conditions of building. Here, especially suitable phase change temperature, large latent heat and large specific heat of PCMs must be considered. Five different types of commercially produced PCMs are experimentally studied in the paper in order to find proper materials for incorporation in lightweight plaster composition. Within the DSC analysis, the researched materials are exposed to the temperature loading from -10°C to 60°C, with temperature change rate of 1, 5, 10, and 20°C/min. On the basis of DSC tests, temperature of phase change and heats of fusion and crystallization are accessed. The obtain data gives clear evidence of the effect of heating and cooling mode on materials performance, because of significant shift of DSC curves measured for similar material. This effect is closely discussed and evaluated, and the proper materials for application in light weight plasters are identified.
In this work we explore the relation of the morphology and the apparent viscosity related to standard workflows of emulsions. Different cuts of distilled water 7 to 30 % were mixed with 10000 cSt silicone oil to produce steady emulsions at room temperature. The apparent viscosity was measured with rheometer G2 ARES. The morphology of the emulsions was obtained from the analysis of acquired microscopy digital images. The results were compared with a simple model of probability distribution function where is taking into account the values of water concentration. A human number realistic of water droplets were counted. Also with home-made software the counting of droplets was done. Both methodologies were evaluated for this study. The distribution was re-scaled until the water droplet number that should have in 1 ml of emulsion. The viscosity was obtained through the expression of interfacial area where the physical meaning is the ratio of emulsion's apparent viscosity and the silicone oil apparent viscosity. In a second experiment, for one silicone oil emulsion mixed with one cut of water, a test of viscosity was running for 5 hours and the morphollog was monitored when the viscosity changes. The results of both experiments were compared with the statistical approximation with good agreement.
Interfacial Properties of Tetrahydrofuran (THF) and Their Mixtures with Some Compounds of Industrial Interest: Atomistic and Coarse Grained Molecular Simulation Models

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The accurate description of the phase equilibria and interfacial behavior of tetrahydrofuran (THF) and their mixtures with compounds of fundamental importance in processes related with natural gas hydrates recovery and CO2 storage, among many others, from a microscopic point of view is essential to understand how molecular details determined the macroscopic behavior of these mixtures. We combine the information obtained from the predictions obtained from the well-known SAFT-VR approach (Determination of the global phase behavior of THF + CH4, + CO2, and + H2O binary mixtures using the SAFT-VR approach), also presented in this conference, to determine the thermodynamic behavior of some mixtures containing THF. In particular, in this work we focus on the description of the interfacial behavior of these systems using two alternative approaches, atomistic molecular dynamics (MD) and coarse grained molecular dynamic (CG-MD) simulations. Agreement between the results obtained from different methods, including MD simulations and theoretical predictions from SAFT, and experimental data taken from the literature is analyzed in this contribution.
The speed of sound and density of a new working fluid, 1-chloro-3,3,3-trifluoropropene (R-1233zd (E)), which is a promising working fluid in the field of low-grade heat recovery, are measured. The measurement was conducted at the temperature from 270 K to 390 K while the pressure up to 5 MPa. Before measurement, the platinum resistance and pressure transducer are calibrated to the accuracy of ±0.05 K and ±1 kPa, respectively. In order to validate the apparatus, the speed of sound and density of R134a was also measured. The results of validation experiment were compared with those calculated from REFPROP. The sonic speed sensor and density sensor has the accuracy of 0.1 m/s and 1 x 10^{-4} g/cm^{3}, respectively. The measurement results, which can be used in verifying consistency of developed equation of state, were also compared with those from REFPROP.
Non-Equilibrium Clathrate Hydrate Composition During Crystallization: Experiments and Modelling

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This work is a contribution to the global understanding of the coupling between kinetic and thermodynamic to explain the clathrate hydrates composition during their crystallization from a water liquid phase and a hydrocarbon gas phase. We faced new experimental facts that opened questioning after comparing the classical modeling of clathrate hydrates following the approach of van der Waals and Platteeuw with our experimental data following a new procedure allowing determining the hydrate composition during crystallization and at equilibrium. In our kinetic model, the enclathratation is described by means of a Langmuir absorption where the composition is fixed from kinetic consideration based on the balance between the absorption rate and desorption rate. These rates turn out to become dependent on the gas diffusion around the hydrate crystals, and so, the geometry of the system needs to be taken into account, especially the mass transfer at the Gas/liquid interface. The procedure results in the definition of non-equilibrium hydrate compositions with a new analytical expression for this composition. In this work, our contribution is to extract self-coherent experimental results from literature, and to re-evaluate properly the Kihara parameters. This step implies to compile and implement all the literature data in a database of a modeling program (called GasHyDyn in our study). Then, we can optimize Kihara parameters from a procedure that can be trivial in some cases where literature data are rich enough to optimize directly the parameters. Then, from the comparison of experimental results to the model, we conclude that the experimental protocol can affect the composition of the hydrates, especially if the crystallization is operated near, or far from thermodynamic equilibrium.
Adhesion Behaviors at Hydrate-Water Interfaces

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Current gas and oil production requires exploration of remote locations like off-shore reservoirs as the crude oil and gas resources have been depleted. Harsh conditions of low-temperature and high-pressure at these reservoirs can lead to the formation of clathrate hydrates between water and small gas/organic molecules. The flow assurance issue arising from the hydrate plug formed inside extraction/delivery pipelines imposes major hurdles to the continuous production of gas and oil. Thus, research in the petroleum industry had been focused on inhibiting the formation of gas hydrates. Understanding of the initial hydrate growth, agglomeration, and attachment to surrounding surfaces must be explored through interaction force studies to gain insights for preventing evolution of hydrate plugs. We have proposed a new setup for adhesion force measurements to characterize the interaction behavior of clathrate hydrates and its emulated surroundings. This talk will introduce the updated setup for adhesion force measurements and explain the volume-dependent adhesion behaviors between cyclopentane (CP) hydrate and solution droplet in a CP/n-decane oil mixture by using the z-directional microbalance. The abnormal variations of capillary bridge between CP hydrate and solution droplet due to hydrate formation will also be visualized through an optical microscope and will be directly quantified in a microbalance.

References

Photoacoustic Monitoring of Water Transport Process in Calcareous Stones Coated with Exopolymers

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Bacterial cells are often found embedded in a matrix of extracellular polymeric substances (EPS) and its growing can occur on inert surfaces in a variety of terrestrial and aquatic environments, including submerged artificial substrata, sediments, soils, and rock surfaces [1,2]. This matrix is a complex mixture of macromolecules, primarily composed of polysaccharides but also containing various amounts of protein, lipid, DNA, and vitamins. EPS are important mainly in terms of attachment, nutrient absorption, and protection against desiccation and antimicrobial agents. Also they can interact actively with dissolved ions in aqueous environments and with framework elements in mineral matrices. EPS have a fundamental role due to their adhesion on the surface of stone, inducing changes in transport process when water penetrates inside of the stones. The photoacoustic (PA) spectroscopy technique has demonstrated to be a tool useful in the study of monitoring of transport of water in real time, which allows obtaining the diffusion coefficient to limestone rocks [3]. In this study, the PA had be used to determinate the influence of different types of EPS in the transport water process when are applied in limestone rocks. The study is complemented by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

References

Concentrating solar power (CSP) systems use solar absorbers to convert sunlight to thermal electric power. In CSP systems electricity is generated from mirrors to focus sunlight onto a receiver that captures the solar energy and converts it into heat that can run a standard turbine generator or engine. The operational temperature ranges of materials for solar applications can be categorized as low temperature (T<400ºC). Concentrating solar power (CSP) systems operate at high- and mid-temperatures. The operation of high efficiency CSP systems involves improvements in the performance of the coatings of the solar absorption materials. To accomplish this, new more efficient selective coatings are needed that have both high solar absorptance and low thermal emittance at the operation temperature. One of the best methods for measuring thermal transport properties are based on illumination of the material using a laser beam modulated with a CW signal (CW, Continuous Wave), this is done in order to excite a response in the material examined and through the application of appropriate mathematical and physical models; optical and thermal properties of materials are obtained. In this work photothermal radiometry (PTR) was used to determine optical and thermal properties of materials applied in CSP systems. PTR amplitude and phase lag data were obtained as function of the modulation frequency and temperature of the material under test.
Gold Nanoparticles (AuNPs) Applied in Hyperthermia Therapy

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Clinical hyperthermia treatment consists in local heating of cancerous tissue; this may be achieved by locating metallic particles within tissue susceptible to be heated under the influence of a radiofrequency (RF) or a magnetic field. Furthermore it has been shown that hyperthermia treatments enhances others cancer therapies like chemotherapy or radiotherapy. However, the applications of these heating techniques not guarantee that healthy cells surrounding cancerous tissue are not damaged. A solution that has been recently explored enables precise local heating; subjecting the cancer tissue embedded with nanoparticles to a laser beam whose power and the spot radius are controllable. This procedure can be applied for superficial head and neck cancer. Gold nanoparticles (AuNPs) absorb energy in the ultraviolet (UV) and visible range (Vis); however at these wavelengths the penetration depth of energy is very low. The solution proposed by various authors is functionalized gold nanoparticles to absorb energy in the wavelength of the infrared range (approx. 800 nm). In this work we present the study of the optical and thermal properties of gold nanoparticles functionalized to absorb energy on the infrared range. Samples of AuNPs were heated with a solid state laser ($\lambda = 808$ nm) specific absorption rate (SAR) was obtained as a function of the time of exposure to the laser energy; also reflectance spectra in the UV-VIS-NIR was obtained.
Hydrogen (or syngas) is an environmentally attractive and promising energy carrier transport fuels with a great outlook for growth and application in industrial processes. Hydrogen can also be stored, distributed and used for a variety of technologies. Hydrogen can be produced from a variety of sources such as wind, biomass, nuclear, etc. or by means of solar energy through thermochemical reactions. Solar thermochemical two step cycles are advantageous due to their ease of application to process scale; these cycles involve redox reactions metal oxide type. The development and characterization of the materials employed in chemical reactions to produce hydrogen and materials required for construction of solar reactors are critical to understand the phenomena involved in the process of transferring mass and heat quantity. Solar technology operating in high temperature conditions, such as those required in power generation, demand accurate knowledge of the optical and thermal properties of the materials involved. This knowledge allows to determine the performance of materials, also helps us in developing designs and emissivity heat fluxes that can be used as parameters in computer models to predict the behavior, performance and reliability of systems in the desired temperature range. One of the best possibilities for measuring the properties of heat transfer is based on the photothermal techniques that analyze the radiation emitted by a material when this is illuminated with pulsed or modulated radiation. In this work the laser flash technique for thermal characterization of the properties of materials involved in chemical reactions for the production of hydrogen is used.
Determination of the Global Phase Behavior of THF + CH₄, + CO₂, and + H₂O Binary Mixtures using the SAFT-VR Approach

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The optimization of processes involved in enhanced natural gas recovery from sources as gas hydrates have gained media attention. Tetrahydrofuran (THF)-hydrates are interesting because the presence of THF decreases the hydrate stability pressure by approximately two orders of magnitude [1]. Thus, a preliminary detailed knowledge of behavior of binary mixtures containing water (H₂O), carbon dioxide (CO₂), methane (CH₄) and tetrahydrofuran (THF) plays a central role in this context. In this work, the molecular based Variable Range Statistical Associating Fluid Theory (SAFT-VR EoS [2,3]) has been used to estimate the global phase equilibria diagram of the binary mixtures THF+CH₄, THF+CO₂ and THF+H₂O over the whole composition, pressure and temperature ranges. To describe this complex multicomponent mixtures CO₂ molecule [4] is modelled as two spherical segments tangentially bonded, CH₄ [5] as a spherical segment, and H₂O [6] as a spherical segment with four associating sites to represent hydrogen bonding. For the case of THF, different models have been tested to model the correct interactions with the named substances. For example, a simple spherical segment model of tetrahydrofuran [7] has been used to represent his interaction with CH₄ and CO₂. Nevertheless, a THF molecule modelled as a spherical segment with two associating sites has been used to represent correctly the complex interaction THF-H₂O. The THF+ CO₂, THF+CH₄ and THF+H₂O binary mixtures exhibit type I, type III and type VI behavior respectively, according to the classification of Scott and van Koleonburg. Finally, the SAFT-VR phase binary diagrams predictions three-phase were compared to experimental results.

References

Artificial Neural Networks and the Melting Temperature of Imidazolium- and Ammonium-type Ionic Liquids

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The use of artificial neural networks (ANN) for the correlation and prediction of the melting temperature of ionic liquids (Tm) is analyzed in this paper. In the study 297 selected data of imidazolium-type ionic liquids and 236 ammonium-type ionic liquids were considered. Several network architectures were analyzed for each set of data and results compared with others from the literature. The independent variables considered for training the ANN (those that could have influence on the melting temperature) were: groups forming the molecules, mass of the cation, mass of the anion and mass connectivity index. These properties are easily available or calculated from information available in the open literature. As a measure of the accuracy of the method the average deviation and the average absolute deviation are evaluated. Results of this work and others from the literature indicate that appropriate selection of data, a good combination of architecture and variables can lead to acceptable correlation of data but accurate predictions with ANN are not yet possible. To make progress in this area of estimating Tm of ionic liquids using ANN it is necessary to standardize the experimental determination of this property so good experiments guarantee reproducibility and elimination of wrong data could be done. Also, it is necessary to know better the structure of the ILs, the characteristics of the anion and cation and which are the variables that may affect Tm to define the most appropriate variables for ANN training. With the present data one cannot obtain good results, especially in predicting the melting temperature of ILs using ANN, at least in the way done until now. Literature information and our own studies indicate better experimental data are needed and that chemical descriptors seem to be the way for making progress in correlating and predicting the Tm of ionic liquids.
Natural gas hydrates are viewed as premium fuel for this century, for the cleanly burning and low pollution. Because of permeability is a property of the porous medium and describes the transmissibility with which fluid can pass through the pore structure, permeability is a key parameter for estimating gas production performance and the flow behaviors of the gas and water during dissociation. To study the index properties and seepage properties of the hydrate-bearing porous media, pore network models combined X-ray computed tomography (CT) are proposed to investigate the influence of wettability on permeability and capillary pressure in the hydrate-bearing porous media. Contact angle is the most reliable method for wettability estimation. The results show that porosities calculated using a two-phase flow simulator in the pore network models are in agreement with those calculated using the volumetric method. The properties of pore networks, such as the average pore radii and the average throat radii, are calculated as well. Moreover, at the same water saturation, the increasing advancing contact angle decreases the capillary pressure of the hydrate-bearing porous media. In addition, at the same water saturation, the increasing advancing contact angle increases the water relative permeability and decreases the gas relative permeability.
For thermophysical property measurements, one typically uses the purest samples available. However, there are circumstances where the use of a lower purity sample is advantageous. Perhaps the best example of this is when measurements are made near the limit of a sample’s stability. In this situation, more accurate results may be obtained by the purposeful addition of an impurity that decreases the extent of sample decomposition during the measurement. We will illustrate such a case for vapor pressure measurements that were made by gas saturation. The gas saturation technique is based on the saturation of a carrier gas stream with the vapor of a condensed phase. The vapor is then stripped from a measured volume of the saturated carrier gas, the amount of vapor is determined, and the vapor pressure is calculated by assuming ideal gas behavior. One important advantage of the gas saturation method is that impurities have a relatively small and predictable effect on the measured vapor pressures. In our apparatus, the carrier gas flows through a series of eighteen “concatenated” saturator-adsorber pairs. In this way it is possible to make eighteen simultaneous vapor pressure measurements. By use of this apparatus, we were able to compare simultaneously measured vapor pressures for oxidatively unstable compounds with and without antioxidant additives. We also simultaneously measured the vapor pressure of an $n$-alkane control sample with a well-known vapor pressure curve.
CO₂-oil Minimum Miscibility Pressure (MMP) is the key parameter for the design and operations of successful CO₂ miscible flood project. The study objective is to develop mathematical models of predicting pure CO₂-oil MMP. Part-1 of the study consisted of the experimental work based on the Rising Bubble Apparatus to measure CO₂-oil MMP for different Omani light oil reservoirs and part-2, contained the development of mathematical models by using the Artificial intelligence techniques based on the resulting MMP values obtained from the experimental work in Part-1 and the literature MMP data. The Artificial intelligence techniques utilized the Artificial Neural Network (ANN) and the Particle Swarm Optimization (PSO) methods. The resulting percent deviations of 4.69 and 4.33 were achieved by using the developed ANN and PSO models for the Omani oil samples MMP data respectively. Thus, the developed ANN and PSO models resulted in more accurate predictions of CO₂-oil MMP than the literature models. The ANN and PSO models were constructed based on the approach that the literature CO₂-oil MMP data were used for the training process of the models and the experimental CO₂-oil MMP results for the Omani oil samples were utilized for the testing of models. This gives an advantage to the developed ANN and PSO models that they are capable of being applied for Oman light oil reservoirs and more widely. The developed mathematical models provide an accurate and fast method for the prediction of CO₂-oil MMP.
Characterization of Glass Micropipette Thermal Probes for Scanning Thermal Microscopy

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Thermal probes have been used in atomic force microscopes (AFMs) to make measurements at the nanoscale. Scanning thermal microscopy (SThM) techniques can use thermal signals to make measurements of both topography and thermal properties. Key to quantifying these techniques is an understanding of the tip properties. Wollaston wire probes and thin-film batch-microfabricated probes have both been widely studied. However, the glass pipette tips from Nanonics Ltd. have not been thoroughly characterized. This work focuses on several important aspects of the tip: amplitude and phase response of the tip as a function of the AC power source frequency, higher harmonic responses, tip signal as a function of sample thermal conductivity, and a comparison of responses in both ambient conditions and vacuum. Scanning electron microscopes (SEM) images will be taken of the nano-tips for tip geometry characterization. Several tips will be analyzed to determine the consistency of the manufacturing process in producing similar characteristics among tips. These measurements will help increase understanding of measurements performed using these unique tips, and allow for more focused research plans.
Equations of State and Phase Transformations of Metals Over a Wide Range of Temperatures and Pressures

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Modeling of thermodynamic properties of substances in a broad region of the phase diagram is interesting as for basic research as for applications. Simulations of hydrodynamic processes in condensed media at intense influences require equations of state for structural materials over a wide range of thermodynamic parameters from normal conditions to extremely high values of temperatures and pressures. Proper inclusion of phase transformations is important from the standpoint of interpretation of those processes. In the present work, a semiempirical equation-of-state model, which takes into account polymorphic transformation, melting, evaporation, and ionization effects, is proposed. Multiphase equations of state for some metals (aluminum, tantalum, tungsten, titanium, iron and others) are constructed on the basis of developed model. Calculation results are compared with available experimental data for the metals at high temperatures and pressures. The most essential static-compression and shock-wave experiments are described.
Thermophysical Property Reliability Issues in the Context of Automated Consumption

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Development of empirical and semi-empirical correlations and models, including force fields, is a data-intensive task. Such activities are frequently performed presuming an error-free set of targets, ignoring ordinary experimental uncertainty, possibility of misreported information, and from where a particular recommended value was ultimately derived. This point is emphasized by the large number of correlations in the open literature which report single-value deviation metrics from target collections which are substantially smaller than achievable experimental accuracy. The required effort to effectively curate an experimentally derived optimization targets is not insubstantial: exponential growth in publication rates and data generation in thermophysical properties has yielded tremendous challenges as well as potential rewards for data analysis groups. Data volumes have grown to such a degree that many traditional data collection and interpretation approaches cannot scale to remain comprehensive and current, to track shifting interests within research and industrial communities, or to effectively filter erroneous data from input streams. It is thus necessary to rely on a substantially increased role for digital archives, automated analysis and machine learning approaches. The approach adopted at the Thermodynamics Research Center (TRC) at the National Institute of Standards and Technology (NIST) is dynamic data evaluation, whereby a reliable and comprehensive data archive is used in conjunction with an algorithmically-encoded expert analysis in order to generate up-to-date property recommendations. These efforts have facilitated a decade's long collaboration with five major journals which report thermophysical and thermochemical property information, where reported data are vetted for consistency by TRC before being made available in a free and open context. This collaborative effort has yielded the unexpected statistic [1] that roughly 20% of published manuscripts have major errors in data or metadata independent of uncertainty characterization. Statistical analysis of error rates and types in analyzed manuscripts will be discussed, with a particular emphasis on potential impacts in the context of machine learning and other data-hungry technologies applied without significant data discrimination.
To slow down global warming there is an increasing focus on reducing carbon dioxide (CO₂) emissions to the atmosphere. Geologic storage of CO₂ is one method that can contribute to nations reaching the desired limits on emissions of greenhouse gases. Long-term storage of CO₂ in geological formations requires knowledge on several different trapping processes that run on different time-scales. In order to understand these complex systems on a field-scale, it is important to understand the nanoscale behavior. Among other, how the solubility trapping of CO₂ occurs. Dissolved CO₂ can react with reservoir rocks and form carbonate minerals. This process is known as mineral trapping and is the most stable form of storage. But insight into the microscopic effects that governs the macroscopic thermodynamic observables can often be hard to obtain, especially when it comes to interfacial systems. We have used molecular dynamics (MD) and focused on carbon dioxide and water adsorbed on calcite. The system consisted of a calcite slab with the (1014) surface exposed to a water phase interacting with a super-critical CO₂ phase. The effect of varying temperature was also investigated through several large-scale simulations at different temperatures. Results show that the density of water increases towards the mineral surface. This creates voids that can facilitate increasing dissolution of CO₂ into the water phase.
Van der Waals Transport Equations of State for the Continuity of Gaseous-Liquid States of Viscosity and Thermal Conductivity

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According to the review of liquid viscosity by Brush (1962), “there is no general agreement on whether viscosity is essentially due to the attractive and repulsive forces,” but on macroscopic scale both viscosity and density are function of the thermodynamic equilibrium state of the fluid (so, both surrender to the Law of Corresponding States) while on micro-scale both properties reflect the effects of molecular motion and interaction. As the efforts on the correlation, prediction, estimation and statistical computation of transport properties have lag behind the efforts on the experimental measurements of transport properties, the methodology of the Van der Waals Transport Equation of State may provide another aspect of predicting and estimating gas and liquid transport properties for pure substances and mixtures by linkage to accurate cubic equation of state for the coexistence gas-liquid densities. Agreeing to the hypothesis articulated by Phillips (1927) and later improvements by Little-Kennedy (1966) and Lawal (1986), a method is established for predicting dynamic viscosity (η) and thermal conductivity (λ) over the entire PVT states of single-phase fluids for such substances as polar and nonpolar, inert gases (argon, helium, xenon), hydrocarbon, non-hydrocarbon (nitrogen, carbon dioxide, hydrogen sulfide) and petroleum and high-molecular-weight fluids. By using the 1986 formalism of the Van der Waals Transport Equation of State (VTEOS) development and on the basis of the phenomenological similarity between PVT and TηP (or TλP) spinodal graphs, accurate coexistence gas-liquid transport properties from dilute-gas to dense and supercritical fluids are predicted without resorting to the judicious choice of liquid density correlation or any volumetric or transport properties. The recently reformed four-parameter cubic equation of state which is valid over the entire PVT states, include the vapor-liquid critical point is used in the development of the VTEOS. The prediction of accurate dynamic viscosity and accurate thermal conductivity demonstrates the versatility of the approach of the VTEOS.
The ideal gas heat capacity of potassium atoms is calculated to high temperatures using statistical mechanics. Since there are a large number of atomic energy levels in the Boltzmann sum below the ionization potential, the partition function and heat capacity will become very large as the temperature increases unless the Boltzmann sum is constrained. Two primary categories of arguments are used to do this. First, at high temperatures, the increased size of the atoms is used to constrain the sum (Bethe procedure). Second, an argument based on the existence of interacting ions and electrons at higher temperatures is used to constrain the sum (ionization lowering procedure). These two methods are both used, and contrasted, for potassium atoms. When potassium atoms are assumed to constitute a real gas that obeys the virial equation of state, the lowest non-ideal contribution to the heat capacity depends on the second derivative of the second virial coefficient, B(T), which depends on the interaction potential energy curves between two potassium atoms. When two ground state (2S) atoms interact, they can follow either of two potential energy curves. When a 2S atom interacts with an atom in the first excited (2P) state, they can follow any of eight potential energy curves. The values of B(T) for the ten states are determined, then averaged, and used to calculate the non-ideal contribution to the heat capacity.
Thermally-responsive polymer particles are capable of changing their shapes given external stimuli, which hold significant promises for a range of applications. Hydrogel particles are the most common type of stimuli-responsive particles that display volume-phase transition (VPT) in water. In response to temperature change, these crosslinked polymer particles can swell or expel water, inducing large volume change. The limitations of hydrogel particles are such that VPT can only occur in the presence of a solvent, and incapable of shape change under constant volume. In this study, we report a new approach to fabricate stimuli-responsive polymer micro- and nanoparticles, capable of demonstrating large shape changes while maintaining constant volume under solvent-less conditions and assess the ability of particles to recover their permanent shape during annealing. Our approach is to use nanoimprint lithography (NIL) to program large deformations into crosslinked polymer micro- and nanoparticles, which can then recover their original shapes upon heating. This talk covers our recent work characterizing the shape memory behavior of these particles throughout the shape memory cycle. In particular, we examine the effects of particle properties (size and crosslinking density), particle-substrate contact, and confinement effects of thin metal layers on the kinetics and morphological evolution of particles during the shape memory cycles. Furthermore, we show that under the thin-metal film confinements, the recovery of the programmed polymer particles can lead to a range of hierarchical wrinkling/folding structures atop the particles. The morphology of the wrinkled/folded metal/particle systems can be controlled via the programming of the polymer particles, thickness of the metal films and the particle sizes.
A generalized cubic equation of state (EoS) to describe vapor pressure and liquid densities of polar and non-polar substances is developed. The EoS is based on the Peng-Robinson pressure-volume-temperature relationship, the alpha function of Heyen and it is a two-parameter EoS in terms of the critical temperature, the critical pressure, the acentric factor and the polar factor of Halm-Stiel. The EoS was developed using two vapor pressure data for 67 highly polar compounds and 23 n-alkanes. To validate the EoS, vapor pressure was calculated for 181 polar and 82 non-polar compounds. The average absolute relative deviation obtained is 1.51%. In total, 8463 vapor pressure were calculated for polar substances and 2300 for gases and hydrocarbons. The EoS was compared with a modified Patel-Teja (PTH) EoS that requires substance-dependent parameters, the Peng-Robinson (PR) EoS and a generalized version of the Peng-Robinson-Stryjek-Vera (PRSV) EoS. Results show that the new EoS is superior to the generalized EoS and it is similar to the PTH EoS that only correlates the experimental data. The deviations are 6.18%, 6.66% and 1.27% for the PR, the PRSV and the PTH EoSs. Additionally, to improve liquid densities estimations, the EoS was translated in volume using one saturated liquid volume. The translation-parameter was generalized for gases and hydrocarbons and it was estimated for polar compounds. Saturated liquid densities calculations were performed for 285 substances and deviations are below 2.8%. Similar values correspond to the PTH EoS. Finally, single-phase density calculations including pressures above 100 MPa were performed for 13 alkanes. Results are better with the proposed model, especially for heavy hydrocarbons. For example, the deviation for n-tetracosane is 6.2% using the proposed EoS while for the PR and the PTH are 44.8% and 13% respectively. Similar results are obtained for other compounds like n-eicosane and n-octacosane.
A Simple and Generalized Model to Represent the Vapor-Liquid Equilibria and the Liquid-Densities of Alcohol-Alkane Binary Mixtures

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A simple model based on a two-parameter cubic equation of state translated in volume and the Huron-Vidal-NRTL mixing rules were developed to describe vapor-liquid equilibria and liquid densities of alcohol-alkane mixtures. To get a semi-predictive model, generalized expressions in terms of critical pressure and critical temperature of alkanes and alcohols were developed for the NRTL binary interaction parameters \( A_{12}, A_{21}, a_{ij} \). The model was proposed employing the homologous series concept as follows: in first place, for 4 series composed by an alcohol between ethanol and 1-pentanol with some n-alkanes between butane and n-undecane, linear generalized expressions in terms of the ratio \( RT_c/P_c \) of n-alkanes were developed for \( A_{12}, A_{21}, a_{ij} \) in each series. The parameters of the generalized expressions were determined minimizing the total absolute relative deviation in bubble pressure. In second place, the parameters of all the series were correlated as quadratic functions in the \( RT_c/P_c \) ratio of alcohols. In total, 22 mixtures were used to develop the model and the average absolute relative deviation in bubble pressure (AADP) estimated is 1.65%. Also, the average absolute deviation in the vapor phase molar fraction (DY) is 0.007. Additionally, to validate the model, predictive calculations were made for 31 binary mixtures that include branched alcohols and branched alkanes. In general, predictions are adequate and results are similar to those reported in literature by associating models like the CPA, the SAFT and the GCA equations of state. The AADP for the new model is 2.80%, while the DY value is 0.009. Finally, liquid densities predictions were performed for 22 alcohol-alkane mixtures and it was found that calculated values are in good agreement with experimental data. The average absolute relative deviation calculated in liquid density is 1.16%. In total 645 densities and 1030 bubble pressures were predicted satisfactorily with the proposed model.
Variation of directional emissivity upon emission angle can be deduced theoretically from the complex refraction index. Nevertheless, theoretical relations are only valid for perfectly smooth surfaces and homogeneous materials. Directional emissivity is generally nearly constant for emission angles lower than 60 degrees from the normal incidence, but strong variations are expected for angles higher than 60 degrees either for dielectric materials or for conducting ones. Many experimental devices were developed to determine directional emissivity of materials. Generally, these devices are quite complex and fail in measuring directional emissivity for angles greater than 80 degrees. Thus, it is still difficult to point out deviations between theoretical and experimental values for high emission angles. Current work concerns the development of a device (SPIDER Instrument) allowing to determine directional emissivity of dielectric or conducting materials. The rear face of the sample is heated periodically. Temperature variations are recorded using a thermocouple. Sample surface temperature variations are recorded using an infrared camera. By comparing at several frequencies and emission angles, the temperature amplitudes recorded, it is possible to determine relative variations of directional emissivity. If directional emissivity is known at a given emission angle, then directional emissivity can be calculated at any emission angle.
Solubility of Unsaturated and Branched Hydrocarbons in Imidazolium Based Ionic Liquids

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Different families of simple gaseous solutes, alkanes[1] or perfluoroalkanes[2], have been used to probe the local structure and molecular interactions in solutions of ionic liquids based on alkylimidazolium[1] or tetraalkylphosphonium[2] cations. For example, from the study of the dissolution of alkanes in imidazolium-based ionic liquids, two conclusions could be upheld: larger gaseous alkanes are more soluble as they interact more favourably with the non-polar side chains; the gaseous solutes are more soluble in ionic liquids with longer alkyl-side chains because they are more mobile in the media and the solvation is entropically more favourable. We present a study of the solubility of n-butane and 2-methylpropane (isobutane) and of ethane and ethylene in 1-alkyl-3-methylimidazolium based ionic liquids. The influence of several structural features on the solvation properties could be assessed: the branching[1] and unsaturation[3] of the solute gas and the size and nitrile functionalization[3] of the ions. For example, it was observed that the solubility of isobutane was lower than that of n-butane in all the ionic liquids and that ethylene was more soluble than ethane in all the studied solvents. The differences encountered are rationalized in terms of the molecular interactions involved in the solubilisation process.

References

The purpose of our work is to achieve a better understanding of the coupling between adsorption and swelling in microporous materials. This is typically of utmost importance in the enhancement of non-conventional reservoirs or in the valorization of CO2 geological storage. We consider here the case of fully saturated porous solids with pores down to the nanometer size (≤ 2nm). Hardened cement paste, tight rocks, activated carbon or coal are among those materials. Experimentally, different authors tried to combine gas adsorption results and volumetric swelling data, especially for bituminous coal. However, most results in the literature are not complete in a sense that the adsorption experiments and the swelling experiments were not performed on the exact same coal sample [1]. Other authors present simultaneous in-situ adsorption and swelling results but the volumetric strain is extrapolated from a local measurement on the surface sample or by monitoring the two-dimensional silhouette expansion [2]. This paper aims at presenting a new experimental setup dedicated to in-situ and simultaneous adsorption-induced swelling measurements in microporous materials. The setup couples a home-built manometric apparatus for gas adsorption measurements and a digital image correlation setup for full-field swelling measurements. Experiments have been performed on activated carbon fully saturated with CH4 and CO2 at 30°C and up to 120 and 50 bars respectively.

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References

The purpose of our work is to achieve a better understanding of the coupling between adsorption and swelling in microporous materials. This is typically of utmost importance in the enhancement of non-conventional reservoirs or in the valorization of CO2 geological storage. We consider here the case of fully saturated porous solids with pores down to the nanometer size (≤ 2nm). Hardened cement paste, tight rocks, activated carbon or coal are among those materials. Theoretically, most continuum approaches to swelling upon adsorption of gas rely on a coupling between the adsorption isotherms and the mechanical deformation. A new poromechanical framework [1] has been recently proposed to express the swelling increment as a function of the increment of bulk pressure with constant porosity. This framework has been extended recently to take into account the porosity evolution upon swelling [2] for simple porosity media. This paper aims at presenting an extended poromechanical framework where the porosity is variable upon swelling. The framework is derived for both simple or double porosity media. A new incremental nonlinear scheme is proposed where the poromechanical properties are updated at each incremental pressure step, depending on the porosity changes. Interactions between swelling and the adsorption isotherms are examined and a correction to the classical Gibbs formalism is proposed. Predicted swellings are compared with results from the literature and with our own experimental database.

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References

The work presented here is a new experimental study on pre-condensation phenomena in an Argon gas-filled quasi-spherical cavity, i.e. the walls of the cavity are coated with a film of condensed Argon even though the saturation point is not reached. Measurement are made at a temperature near 88 K and a pressure near 108 kPa, under adiabatic conditions and using accurate metrological instruments. The effect of pre-condensation is measured by a change in the acoustic resonance properties (resonance frequencies and halfwidths) of the resonator. Simultaneously, the microwave resonances of the TE11 mode and the TM11 triplet are also measured. From the relative change of frequency of these microwave modes we extract the thickness of the condensed film. The experimental set-up is based on that we have used to determine the Boltzmann constant and represents the state of the art for control of pressure and temperature. In contrast to other experiments on pre-condensation, the gas pressure is kept constant by the use of a piston gauge and the temperature is decreased and increased only slowly. The experimental results will be compared with those obtained using an analytical model for the acoustic field in the resonator that describes the strong coupling between acoustic motion, pre-condensation processes and thermal effects in the boundary layers (Phys. Rev. E 89, 023208 (2014)). This model builds upon that developed by Mehl and Moldover (J. Chem. Phys. 77, 455 (1982)). The results of this study should be of interest for primary acoustic thermometry, studies of thermophysical properties of gases and other applications such as thermoacoustic engines or propagation in wet granular media.

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Acoustic and Microwave Resonance to Probe Pre-Condensation Phenomena in Argon
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The phase behavior of (binary) polymeric solutions such as lower critical solution temperature (LCST) plays a significant role in various polymeric processes. For theoretical investigation on the prediction of LCST, a substantial data points on LCST of binary polymeric solutions were collected from literatures and used to (i) develop an efficient and accurate empirical correlation for LCST estimation through statistical modeling using matrix algebra (namely M1) and also (ii) to present a reliable calculation routine through chemical engineering thermodynamic approach (namely M2). To develop the statistical model (M1), the connectivity indices of polymer and solvent were used as the independent variables in M1. The thermodynamic models of Nonrandom Two Liquids (NRTL), Universal Quasi-Chemical (UNIQUAC), Flory-Huggins (FH), Modified Separation of Cohesive Energy Density Model (MOSCED) and Compressible Regular Solution (CRS) were studied in presentation of chemical engineering thermodynamic approach (M2). Four statistical parameters i.e. Sum of Squares due to Error of the fit (SSE), the Square of the correlation (R-2), adjusted R-square (R2-adj) and Standard Error of the Regression (RMSE) were defined as criteria to evaluate the models and convergence of calculations. The minimization of errors and objective functions was done by applying Particle Swarm Optimization (PSO) algorithm. The reliability and accuracy of proposed approaches discussed in details and the results were compared to the available experimental data and the reported results of quantitative structure–property relationship (QSPR) approach.
Asphaltenes are the heaviest and most complex fraction of the crude oil. They are polydisperse and are defined as a solubility class which is soluble in aromatic solvents and insoluble in n-alkanes. Asphaltenes can precipitate and deposit in wellbores due to changes in temperature, pressure and composition. Such asphaltene deposition problems reduce the oil production and cost millions of dollars in mitigation and remediation efforts. Our group focuses on the development and implementation of advanced thermodynamic models and experiments to address the thermo-physical characterization and the phase behavior of crude oils in general and asphaltene precipitation in particular. Solubility parameter significantly influences the asphaltene precipitation behavior and is therefore a critical parameter in the context of understanding flow assurance issues related to asphaltenes. This work focuses on the exploration of the solubility behavior of asphaltenes in various model crude oil samples at a molecular level by calculating solubility parameters of the mixtures over a wide range of temperatures and pressures. Based on previous work, the solubility parameter can be correlated with the density and the refractive index at ambient conditions. By measuring the density and the refractive index data, experiments can be executed to evaluate the solubility parameter at ambient conditions. Using this information and advanced equation-of-state modeling, solubility parameters over a wide range of temperatures and pressures (covering reservoir/wellbore conditions) are calculated and will be presented. Molecular dynamics simulations in predicting solubility parameter values of solvent mixtures and asphaltene molecular models under reservoir conditions will also be presented.
Nuclear waste vitrification in the UK sees a radioactive waste calcine combined with a borosilicate glass frit, and mixed in an induction melter at temperatures typically up to 1300 K before transfer to containers for storage and eventual disposal. Viscosity is a critical process parameter in this operation; too high and the melt will not mix or pour correctly into the containers, too low and the temperature can lead to volatilisation or the generation of unwanted refractory oxides. Understanding the effects of compositional changes on viscosity is therefore important in predicting melter operations. However, direct viscometry testing of all of these glasses is impractical on account of their radioactivity, inventory and uncertainty due to changing compositions as plants are being decommissioned. Here we describe how we have applied modelling and simulation to develop models to predict viscosity in these materials. The approach taken has been to utilise modelling and simulation across different length and time-scales in order to predict viscosity and understand the implications for plant performance. In the first part we will describe how we have utilised experimental data for inactive simulant nuclear waste glasses supplemented by the theoretical modelling semi-empirical, to predict the temperature-viscosity behaviour of different melts, including the data fitting methodology and model validation. In the second part we will describe how we have tested a molecule dynamics approach to calculating these properties from first principles, and describe the challenges and successes from computational and a physical model perspective. This work includes an assessment of equilibrium and non-equilibrium simulation approaches to calculate viscosity and a critical review of the empirical potential literature for borosilicate glasses. Finally we will describe how we are utilising this data in CFD models of the process.
Ultrasound is widely used for imaging, measurement and diagnostics in the MHz region and is very familiar as a powerful medical diagnostic tool but also finds widespread application in engineering as a non-destructive testing tool. Typically ultrasonic wavelengths are in the mm-micron range, many times longer than the wavelength of visible light which limits the resolution that these systems can achieve. By using acoustic waves in the GHz region, it is possible to perform ultrasonic imaging and measurement using ultrasound with wavelengths less than that of visible light and, potentially, to achieve higher resolution than optical microscopy. However, as the frequency of the ultrasound goes up the attenuation rises steeply and it becomes a considerable technical challenge to generate and detect the acoustic wave with sufficiently signal-to-noise ratio to permit measurement and imaging. Despite this nanoscale ultrasonics has much to offer as a powerful diagnostic tool. In this paper we discuss some of the practical problems standing in the way of nano-ultrasonics and some of the solutions, especially the use of picosecond laser ultrasonics and development of nano-ultrasonic transducers\[1\] using layered and nanoparticle structures. We present experimental results showing the measurement of protein adhesion and imaging on cell phantoms and 3T3 fibroblast cells.

References

Viscosity and density are thermophysical properties required in many applications within the petroleum industry. In the past, the friction theory (FT) approach has proven to accurately model the viscosity and density of a wide variety of reservoir fluids ranging from natural gas to heavy oil. The FT approach consists of a compositional characterization method, an applicable Equation of State (EoS) (such as a cubic EoS) and an EoS based FT viscosity model. This combination of these three methods is capable of delivering an integrated approach for the accurate description of the phase, PvT and viscosity behaviour of reservoir fluids. The updated model presented in this work extends the FT approach to larger compositional, temperature and pressure ranges compared to previous work. Combined with continuous thermodynamic principles, the new FT modelling approach can be easily applied to areas that require computational efficiency, as in the case of flow simulations, or which require high compositional accuracy, such as distillation. The applicability of the FT models has also been extended to ranges of viscosity which vary from single digit mPa’s up to hundreds of thousands. The new approach has also been improved to deliver accurate predictions of blend properties. In this presentation, results from the FT modelling approach will be summarized and discussed for a variety of reservoir fluids.
Implementation of Isochoric Slopes for Mixture Properties Calculations

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The physical properties of fluid mixtures have been a research focus for more than a century. Some important reasons were and continue to be the need for efficient and economical industrial processes, engineering design calculations and purely scientific curiosity. Accurate prediction of physical and calorimetric properties of fluid mixtures by an equation of state requires an accurate description of the effects of intermolecular forces between both like and unlike molecules. The effects of the unlike interactions are especially challenging, because they exist only in mixtures, and they may have strong composition dependence. Experimental measurements for mixtures are necessary, and the number of measurements required should be minimized. Experimental measurements of derivatives such as $\partial P/\partial T$ have been used previously to evaluate the thermodynamic consistency of equations of state and the impact of using numerical and analytical derivatives during equation development. In this work, we have explored, using different sets of data covering wide pressure and temperature ranges, the use of isochoric slopes ($\partial P/\partial T$) obtained from PpT measurements to develop correlations that improve the predictions of excess properties. Isochoric slopes are attractive for this application, because they are directly related to energy and entropy calculations, and they depend strongly upon composition but weakly upon temperature in the single-phase region. The excess properties are calculated using properties for pure substances calculated using reference equations of state and mixture properties that have been measured experimentally. The predicted mixture properties then are compared to experimental data.
We have investigated the thermal radiation properties of a crystal self-assembled with silica particles of 3-5 micro meter diameter. The thermal radiative properties of a self-assembled photonic crystal with defects were different from those of a perfect photonic crystal in our previous numerical work using RCWA method. The enhancement of normal spectral absorptance was shown only for the photonic crystal with defects in the calculation result. The emittance is the same as the absorptance according to the Kirchhoff's law. For the verification of the simulation result and exploration of the mechanism of the absorptance enhancement, we developed a measurement system for thermal radiative properties of the fabricated photonic crystals. In this study, we measured the normal spectral emittance and the normal-hemispherical spectral reflectance of the fabricated silica photonic crystals by a FTIR with paraboloidal mirror. We also measured the normal-hemispherical spectral reflectance of the sample using an integrating sphere reflectometer to confirm the measured results. The self-assembly fabricated photonic crystal was heated up to 523K for the emittance measurements using a FTIR. The normal-hemispherical spectral reflectance was measured by using an integrating sphere reflectometer to confirm the validity of the normal spectral emittance measurement. The measured normal spectral emittance of the photonic crystals of silica particles in 3 micro meter diameter was increased in the vicinity of 3 micro meter. The measured enhancement was agreed well with the results numerically calculated by RCWA method. The measured normal-hemispherical spectral reflectance was decreased in the same wavelength. The validity of the normal spectral emittance measurement by FTIR was confirmed. The normal spectral emittance can be enhanced by using the photonic crystals with defects, although such enhancement in the emittance cannot be expected in the perfect photonic crystals.
Thermomechanical Responses of Porous Polymer Membranes During the Nanoimprint Process and Their Influences on the Permselectivity of the Membranes

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Recent studies have shown that sub-micron surface patterns can be directly imprinted onto the surface of porous polymeric membranes under compression at a temperature below the glass transition temperature (Tg) of the polymer. Initial results demonstrated that the presence of these patterns improves the antifouling characteristics of the membranes during separations with feed solutions containing colloidal particles or proteins. A more comprehensive understanding of the influence of the imprinting process on thermomechanical deformation is essential since deformation at various combinations of temperature and pressure dictates the characteristics of the final porous structure and thus membrane performance (permselectivity). In this study, we present results from systematic measurements obtained from conventional mechanical testing (tensile and dynamic loading) as well as nanoscale thermoanalysis (nano-TA) of ultrafiltration (UF) membranes before and after nanoimprinting. This work compares data from two commercial polyethersulfone (PES) UF membranes: one of which consists of a small-pore thin layer atop a larger-pore support layer and the other adds both macrovoids as well as a backing layer. Each membrane was plastically deformed at various combinations of pressure (P) and temperature with P < 4 MPa and T < Tg, and the results show that the temperature dependence of the yield strength agrees well with that predicted for open-cell foams. Pore-size measurements determined by electron microscopy and evapoporometry indicate that the pore-size distribution becomes narrower due to the elimination of the largest pores during compression. Thus the imprinting process effectively reduces the structural hierarchy. Moreover, the relationship between PSD and membrane performance as a function of pressure and temperature indicate that systematic effects are surprisingly modest.
L-ascorbic acid is a water-soluble vitamin, known as vitamin C, which plays an important role as antioxidant in humans due to its ability to reduce chemicals like free radicals avoiding that other vital molecules can be oxidized during the normal or pathological cell functioning. This ability of vitamin C has been used to perform spectrometric techniques to quantify its concentration by reducing colored chemicals giving an uncolored compound. One of these compounds is methylene blue, which is a water-soluble dye. The reaction of methylene blue with L-ascorbic acid produces a colorless hydrogenated molecule leucomethylene blue. Therefore, this reaction permits to quantify the vitamin C by spectrometric techniques in low absorption coefficient samples. The objective of the present work was to compare the utility of UV-vis spectroscopy versus the thermal lens spectroscopy to monitor the photodegradation process of vitamin C induced by visible or UV light, as well as the production of the degraded products measured by HPLC. In this work, the photodegradation process of vitamin C was studied using a fixed concentration of vitamin C dissolved in HPLC grade water. Samples of vitamin C were illuminated with visible, UVA or UVB light, while an additional group of samples were kept in dark. Several aliquots were taken at different times during the illumination period and for samples kept in dark to monitor the photodegradation process. This event was studied using UV-vis spectroscopy and the potential of thermal lens spectroscopy by adding the aliquots to a fixed concentration of methylene blue previous to the measure. Otherwise, quantification of the main degraded products of vitamin C were measured by HPLC.
Vitamin E is a liposoluble substance in which its most biologically active component is alpha-tocopherol, due to its capability of capturing free radicals and breaking lipid peroxidation chain reactions, and as a consequence preventing the destruction of lipids. Photo-oxidation of alpha-tocopherol is a big concern because their degradation products not necessarily have the same beneficial effects than intact vitamin. Due to the handling and storage of this vitamin, it is important to evaluate the effect of sunlight on the stability of alpha-tocopherol, having at hand methods with enough sensitivity to evaluate the effects of photons of different energy. Thermal lens has been shown to have very high sensitivity, being able to detect even traces in liquids [1]. In this work, the capability of the thermal lens technique to detect minimal changes during UV induced photodegradation of alpha-tocopherol and its reaction products is explored. Thermal lens measurements of the degradation process were measured using two lasers one at 488nm and the other at 638nm. The kinetic process was also studied by liquid phase chromatography and UV-Vis spectroscopy.

References

Nanoscale Patterning of Self-assembled Monolayer on Membrane Structure by Near-field Photothermal Desorption

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We have developed a nanoscale patterning method of a self-assembled monolayer (SAM) by using a near-field light. SAM is an organic thin film which is formed on a substrate surface, and surface characteristics can be changed easily. Furthermore, SAM is formed by intermolecular force self-assembly, therefore it has high uniformity and quality. For these reasons, SAM has gained much attention, because of the great potential in various scientific and engineering fields. Hence, we have proposed a non-contact and non-contaminated patterning method of SAM at nanoscale by using near-field photothermal desorption (NPTD). In NPTD method, a short-pulsed irradiation with a near-field light is performed, and the surface is locally heated at nanoscale by photothermal effect. Then, SAM molecule is desorbed from the substrate completely by breaking chemical bondings between SAM and substrate. In this study, near-field light is excited at a tip of the near-field optical fiber with small aperture. In our previous configurations, the temperature rise of sample surface caused by the near-field photothermal effect is not sufficient because of the significant heat loss toward the substrate. When high intensity laser was coupled into the fiber in order to enhance the intensity of the near-field light, the small aperture at the near-field optical fiber was damaged. Therefore, we have proposed a new sample structure which can achieve high-efficient heating of the sample. By adopting the membrane structure, a heat loss can be prevented. A simple preliminary experiment by using the membrane shows a validity of the photothermal desorption of SAM. In addition, the temperature distribution with irradiating near-field light is calculated by the finite difference time domain method. As a result, the surface temperature at the membrane is higher than our conventional configurations, and it shows the feasibility of the nanoscale patterning of SAM by the near-field photothermal effect.
Micro Optical Diffusion Sensor Using Laser-Induced Dielectrophoresis with Sputtered a-Si:H

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The mass diffusion coefficient is size- and construction-dependent parameter, therefore, the diffusion coefficient is a useful parameter for the observation of the conformational change and the bonding behavior of the molecule in the fields of the clinical diagnosis of neurodegenerative disease such as Alzheimer’s disease. Several methods have been developed to measure the diffusion coefficient of the biological sample, however, a sensor applicable to point-of-care testing (POCT) has not been established because of the difficulties due to the requirement of high-speed measurement and small sensing device. In order to realize high speed, additives-free sensing with small sample volume, micro optical diffusion sensor (MODS) has been developed. In the measuring process, the concentration distribution is generated in micro-channel by laser-induced dielectrophoresis (DEP) that is a manipulation technique based on optoelectronic tweezers. For laser-induced DEP technique, a hydrogenated amorphous silicon (a-Si:H) is utilized as a photoconductive layer. In this work, a simple RF magnetron reactive sputtering method was applied as a new method to deposit an a-Si:H on the transparent electrode. Proposed RF magnetron reactive sputtering method is easy-to-use procedure compared with a plasma enhanced chemical vapor deposition using monosilane. The photoconductive layer was sputtered by several conditions, and the photoconductivity was experimentally evaluated. Moreover, the optical and structural property of the sputtered a-Si:H was measured by Raman spectroscopy, Fourier-transform infrared spectroscopy, and ultraviolet and visible spectrophotometer. The DEP cell was fabricated by the appropriate sputtering condition and succeeded in generating a concentration distribution of nano-sample, therefore the validity of the proposed a-Si:H by using the sputtering method has been confirmed. Furthermore, a new DEP cell with the sputtered a-Si:H was proposed. According to the numerical simulation, the force induced by DEP in the newly designed cell can be successfully generated.
Modelling and Measurements of Viscosity and Volumetric Behaviour of Mixtures of Heavy Hydrocarbon + CO₂ at High Pressures.

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The investment in the petroleum industry in projects involving CO₂ is increasing while the impact of CO₂ on global economy is rising steeply. CO₂ is becoming widely used for heavier oil production but the mechanism by which the hydrocarbon rich phase is displaced is not fully understood especially in the miscible and near miscible regimes. Accurate data on viscosity and phase behaviour of mixtures containing hydrocarbons and CO₂ are necessary not only for upstream recovery and production but also for midstream oil and gas pipelines and transport networks and also for downstream separation and chemical process plants including coal bed methane and Natural gas plants where CO₂ co-exists in high proportions. CO₂ is highly soluble in most hydrocarbons at low and moderate pressures where viscosity, and density of the mixture decrease and volume swelling is observed. At high pressure range, density crossover can occur due to the dramatic increase in the density of CO₂ with pressure. For example, at 100 °C, when pressure increases from 2000 to 8000 psi, density of n-decane only increases from 680 to 720 kg/m³ while the density of CO₂ significantly increases from 290 to 850 kg/ m³, crossing over the hydrocarbon density. In such a complex volumetric behaviour a second liquid CO₂-rich phase can also exist. Viscosity of the hydrocarbon is also reduced when mixed with CO₂ and also depends, to a great extent, on pressure. In this work we report measurements on viscosity and volumetric properties for binary mixtures of CO₂ + heavy n-alkanes including isothermal compressibility, mass density, bubble points at temperatures from (313 to 410) K and pressures up to 76 MPa (11000 psi). Our data are compared with the predictions of both theoretically-based equation of state SAFT and PR cubic eos commonly used in software simulators. Excess volume calculations for this mixture are also presented. The accuracy of experimental data and challenges with the experimental technique are also discussed.
Cohesive Energy and Volatility of Protic Ionic Liquids

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Cohesive energies are intimately related with the volatilities of ionic liquids, which may be decisive for their use as replacements of conventional volatile industrial solvents. The determination of cohesive energies of protic ionic liquids (PILs) is, however, a practically unexplored topic. This problem was addressed here by using a combination of calorimetric and high-accuracy explicitly correlated quantum chemistry methods, namely the W1-F12 and CCSD(T)-F12 methodologies. The work involved a series of [HB]A PILs (HB = 1-methylimidazolium, 1-ethylimidazolium, 1-butylimidazolium, 1-octylimidazolium, and 1,1,3,3-tetramethylguanidinium; A = nitrate, chloride, perchlorate, and ethanoate), which are expected to cover a significant range of ionicity, given the differences in acidity/basicity strengths between their acid (HA) or base (B) precursors. The relationship between the obtained cohesive energies, the extent of HA to B proton transfer, and the vaporization channels that are likely to determine the volatility PILs will be discussed.

Acknowledgements

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A formula to calculate lattice volume in nanoscale size crystals free of fitting parameters is derived depending on the maximum increase of mean bond length $d_{\text{mean}}$, melting entropy $S_m$ and critical particles radius. The particle critical radius ($r_c$) is calculated from the values of the first surface atomic layer height symbolized by ($h$). The surface first layer height of atoms $h$ is calculated according to the fitting relation, $h=1.429\, d(\text{mean, for bulk state})$. For InP values of ($h$) and melting entropy ($S_m$) are 0.3775nm and 30.28(Jg-atom$^{-1}$K$^{-1}$) respectively. Size dependent mean bond length can be calculated using the relation $d_{\text{mean}}(r) = h - \text{increase of } d(r)$. Knowing $d_{\text{mean}}(r)$, the size dependent lattice parameter $a(r)$ can be calculated according to the relation $d_{\text{mean}}(r) = [a(r)/4]^{3/2}$ and then the lattice volume $V(r)$, $r$ is the nanoparticles radius. The bulk state for this relation as ($r$ go to infinity) gives values of $d_{\text{mean}}(\text{infinity})$ for seven of binary III-V compounds including AlSb, GaAs, GaP, GaSb, InAs, InP and InSb as interested in this work. The increase of lattice size reaches to about three times of its bulk state when $r$ reaches $r_c$ as $V(r_c)$ for example for InP it reaches to 83 Å$^3$ from its bulk value of 25 Å$^3$. From the values of $V(r)$ calculated according to the information above, the nanoscale size dependence of melting temperature $T_m(r)$ for all compounds are calculated according to the modified model (Omar 2012), depending on the increase of lattice volume $V(r)$, melting entropy, nanoparticles critical radius and the materials bulk melting temperature. The melting temperature decreases with the decrease of nanoparticles size and reaches zero when its radius reaches its critical value ($r_c$). Bulk melting temperature and lattice volume, for InP for example, have values of 1333 K and 25 respectively. From the size dependent melting temperature $T(r)$ and mean bond length $d_{\text{mean}}(r)$, the size dependent lattice thermal expansion LTE($r$) are calculated according to the modified relation reported by (Omar 2012). For all compounds investigated in this work, LTE decreases with the decrease of nanoparticles radius and reaches down to zero for $r$ approaches about 3nm for InP as an example. For other compounds their minimum values higher than zero still they are occurred at the same radius.

References

In this talk we are going to present the conductivity relaxation measurements of a number of ionic liquids (ILs). The dielectric studies of conductivity relaxation were performed as a function of both temperature and pressure. In addition we carried out PVT measurements for all investigated ILs. By combining these two sets of data we were able to analyze density dependence of the conductivity relaxation times and consequently to test the validity of density scaling concept. Moreover the temperature-volume data were analyzed in term of the modified Avramov model. As a result it was pointed out that there is the relation between the electrical transport properties of investigated ILs and their thermodynamic properties, represented by scaling exponent $\gamma$ and Grüneisen constant $\gamma_G$, respectively.
Breast cancer is a predominant cancer worldwide among women. To address this problem, a considerable scientific effort has already been going on round the globe seeking early detection of the disease. Many optical spectroscopy techniques have also been experimented to detect breast cancer early and with reduced costs. Studies based on photoacoustic spectroscopy have shown steady growth and demonstrated enough capabilities to detect the disease early. With the aim to detect breast cancer early, tumor progression in nude mice as xenograft model was studied using a pulsed laser induced photoacoustic spectroscopy. Tumor tissues were extracted from the nude mice xenografts at different time points (10\textsuperscript{th}, 15\textsuperscript{th} & 20\textsuperscript{th} day) post MCF-7 cells injection and the corresponding photoacoustic spectra were recorded at 281nm pulsed laser excitations. There were 144 time domain photoacoustic spectra recorded from 36 tumor tissues belonging to 36 animals, 12 each to the three time point groups (10\textsuperscript{th}, 15\textsuperscript{th} and 20\textsuperscript{th} day post injection). The spectra were then Fast Fourier transformed using MATLAB algorithms for further analysis. The spectral comparison of the inter-day group of animals have shown a distinct pattern in the intensity of peaks at $5.93 \times 10^3 \text{Hz}$, $15.9 \times 10^3 \text{Hz}$, $29.69 \times 10^3 \text{Hz}$ and $32.5 \times 10^3 \text{Hz}$ respectively indicating that these frequencies are more sensitive towards tumor development. Further discrimination analysis of the data also indicated a clear variation in the spectral patterns of the samples belonging to different time point groups under study highlighting the sensitivity of the technique in identifying tumor development and growth. The outcomes of the study clearly demonstrated the usefulness of the technique in assessing tumor development and growth which may have clinical implications.
The Non-radiative Relaxation Time of Barley Seeds (*Hordeum vulgare*)
Investigated by Photoacoustic Spectroscopy

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In processes of laser biostimulation of agricultural seeds, i.e. application of photonic energy into wavelengths and doses specific which produce a macro or micro effect, this bioeffects could be function of the characteristics of the seeds, as is the non-radiative relaxation time [1,2]. Therefore, the objective of the present research was to determine the non-radiative relaxation time (t) of two barley seed conditions: natural seed and dyed seed, at wavelength irradiations (l) of 632, and 650 nm which correspond to the typical lasers used in seeds treatments pre-sowing. The t values were determined by photoacoustic spectroscopy measurements. The obtained t values could be important in the exposition times used in biostimulation by laser irradiation to improve the efficiency of these processes, due to the fact that the cells in the seeds are able to absorb, transform and use the energy of light photons in short times. The non-radiative relaxation [3] time values were correlated with the results found in a physiological quality test where pre-sowing seed was irradiated with laser diode 650 nm.

References

One of the most universal physical processes shared by all matter at finite temperature is the emission of thermal radiation. With its origin in thermally driven fluctuations of charge carriers, thermal radiation reflects the resonant and non-resonant dielectric properties of media, which is the basis for far-field thermal emission spectroscopy. However, associated with the underlying fluctuating optical source polarization are fundamentally distinct spectral, spatial, resonant, and coherence properties of the evanescent thermal near-field. Using scattering scanning near-field microscopy we have been able to spectroscopically and spatially characterize the thermal near-field associated with molecular and surface phonon polariton (SPhP) resonances. In agreement with theoretical predictions we observe a dramatically enhanced electromagnetic local density of states (EM-LDOS) in close proximity to the sample surface. This technique of thermal infrared near-field spectroscopy (TINS) provides for broadband chemical nano-spectroscopic imaging, where the thermally driven vibrational optical dipoles provide their own intrinsic light source. Furthermore, we study the spatial and spectral characteristics of the thermal near-field SPhP response in SiC and hBN. In contrast to the strongly surface-confined thermal near-field of localized vibrational modes, an extended exponential distance dependence reflects the spatial coherence of the SPhP thermal field. The combination of intrinsic materials resonances and extrinsic optical antenna or metasurface modifications provide for local spectral and spatial control of radiative heat transfer or light-matter interaction using thermal near-field radiation.
Mutual Solubility of Water and Hydrocarbons

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The accurate estimation of water-hydrocarbon vapour-liquid and vapour-liquid-liquid equilibrium is an important activity related to safe and reliable design of industrial equipment. Currently heavy, highly aromatic oil fractions are of interest due to the use of bitumen and heavy oil as feedstock and proper estimates for water in hydrocarbon, hydrocarbon in water and hydrocarbon in air concentrations are key parameters for process design and evaluation of new processes such as high temperature thermal upgrading using supercritical water. In addition to heavy hydrocarbon feedstock processing the correct estimation of water solubility in gaseous hydrocarbons as well as in liquid hydrocarbons is of interest for the gas production and midstream industries due to the possibility of gas hydrate formation in pipelines and ice formation in cryogenic distillation towers and the associated safety and efficiency problems. In addition, novel separation processes based on the formation of hydrates and ice require accurate quantitative models that can be used to calculate the amount of solids formed together with accurate fluid phase models for the calculation of water concentrations in the gas and liquid phases at equilibrium. In this paper we present a simple and accurate equation of state model used for the calculation of water solubility in gas or liquid hydrocarbons, solubility of hydrocarbons in water and its use for the calculation of vapour-liquid-solid equilibrium. The model can be used to represent aqueous systems at low and high temperatures, is simple to use, can be used for the computation of consistent phase envelopes and is extensible to other types of mixtures.
Materials with length scales on the order of few nanometers exhibit unique abilities to control thermal transport. Tailoring the thermal properties of nanostructured systems have a promising application in the field of microelectronics and thermoelectrics. In this work, we demonstrate a novel technique using high-pressure torsion (HPT) to create a high density of lattice defects on nanometer length-scales in semiconductor materials such as silicon and germanium. We report a dramatic reduction in the thermal conductivity of bulk crystalline silicon and germanium when subjected to severe plastic strain under a pressure of 24 GPa at room temperature using HPT. Thermal conductivity of the HPT-processed samples were measured using pico-second time domain thermoreflectance. The reduction in thermal conductivity is attributed to the formation of nanograin boundaries and metastable phases which act as phonon scattering sites. Subsequent annealing shows a reverse transformation from metastable phases to cubic diamond phase and a nominal increase in thermal conductivity due to the reduction of the density reduction of secondary phases and nanocrystalline defects.
Density Measurements of Liquid Fe-Ni Alloys Using an Electromagnetic Levitation Technique in a Static Magnetic Field

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Fe and Ni are important constituents for various industrial alloys such as stainless steels, hastelloy, inconel, permalloy, and inver alloys. Each alloy has an excellent property such as high corrosion resistance, high heat resistance, high magnetic permeability or low thermal expansion coefficient. From the practical importance, thermophysical properties of the Fe-Ni melts should be well established. As a first step, we have studied the density of the melts because the density is the most basic property required for measurements of surface tension, heat capacity, and thermal conductivity. Thus, the purpose of this study is to measure the accurate density of the Fe-Ni binary melts using an electromagnetic levitation technique in a static magnetic field. A static magnetic field was employed to effectively suppress the surface oscillation and translational motion of the levitated sample droplet, which enables a high-precision density measurement. This experimental facility is called PROSPECT, which has been designed to measure heat capacity, emissivity, thermal conductivity, density and surface tension of metallic melts with high accuracy in our laboratory. Using PROSPECT, the volume of the levitating sample droplet was measured from the sample images taken by a high-speed camera with a laser back illumination system. The sample temperature was monitored using a pyrometer, and it was calibrated using the liquidus temperatures of the alloy. The densities were measured from 0 to 100 mol% Fe in the Fe-Ni melts. For all compositions of the melts, the densities are expressed with a linear function of temperature. We also determined the molar volume of the melts as a function of composition. It shows a positive deviation from an ideal solution, which indicates that the excess molar volume is positive over the entire range of composition. Details of experimental procedure, results and discussion will be presented in the symposium.
Present steel processing, interfacial phenomena between molten steel and oxides in which are usually called slag or mold flux, play important roles in materials design. For examples, in continuous casting, Marangoni convection due to the gradient of the interfacial tension between molten iron and molten oxide enhances heat transfer, and also avoid drop-off of oxide particles from flux into molten iron. Therefore, interfacial tension must be known for process controlling. From this requirement, we proposed the interfacial tension measurement technique between molten steel and oxides using the modified oscillating drop method with levitation techniques. The interfacial tension data using traditional technique based on the sessile drop method have been obtained only in temperature at melting temperature of iron due to dissolution of containers and the substrate into molten steel and oxides in higher temperature regions. Our propose technique to obtain temperature dependence of interfacial tension between molten iron and oxides is used a core-shell form droplet including interface between two liquids [1] using the electrostatic levitation, which can achieve the containerless conditions. However, since the difference of viscosity of molten steel and oxides are larger, the large viscosity difference affects on the surface oscillation of droplet [2]. Therefore, we performed numerical simulation of droplet oscillation of core-shell drops of molten iron and oxides, and we discussed the best conditions of droplet conditions including the viscosity value range for interfacial tension measurements from the outer surface oscillation frequency. The measurements will start late 2015 in International Space Station (ISS) using the electrostatic levitation furnace (ELF) in KIBO.

References:

Water is an anomalous and unique liquid in the sense that some of its physical properties do not exhibit monotonous behaviour when plotted against temperature. For example, isobaric heat capacity exhibits a minimum near 37 C. No theory/model is available in the literature to explain this behaviour of isobaric heat capacity with temperature. We, therefore, suggest a model to study the isobaric heat capacity of water as a function of temperature. The model is based on two-state theory of water in which water is considered as a mixture of two species. One of the species is called open-packed specie resembling with ice structure and having mole fraction as $X_0$ whereas the other is called closed-packed species resembling with un-hydrogen bonded water molecules and having mole fraction as $X_c=1- X_0$. An empirical relation is developed as a function of temperature for open-packed specie using the data reported by Davis and Litovitz [J.Chem.Phys. 42,2563 (1965)]. On the basis of this mixture model, isobaric heat capacity of water is assumed as $C_P=X_0 C_{p0}+(1-X_0 )C_{pc}$. Furthermore, $C_{p0}$ and $C_{pc}$ are considered as a function of temperature. The computation of heat capacity indicates a minimum near 40 C which is in very good agreement with experimental result.
Accurate thermodynamic modeling of aqueous electrolyte solutions is essential for many industrial applications such as hydraulic fracturing, desalination, nuclear waste management, etc. Requiring only two binary interaction parameters, the electrolyte non-random two liquid (eNRTL) model is capable of representing the liquid phase nonideality over the entire concentration range from pure water to pure fused salt. Another important characteristic of the eNRTL model is the weak temperature dependency of the binary interaction parameters. In this study we investigate the relationship between temperature coefficients of the eNRTL binary interaction parameters and excess molar enthalpy of electrolyte solutions. We show excess molar enthalpy of electrolyte solutions form a simple family of curves as function of electrolyte concentration. We further show the temperature dependency of the eNRTL binary interaction parameters can be expressed in a Gibbs-Helmholtz type expression with three temperature coefficients representing Gibbs energy, enthalpy, and heat capacity contributions. The enthalpy term of the temperature dependency expression has been correlated to excess molar enthalpy of electrolyte solutions for more than 100 electrolytes. The resulting eNRTL model and model parameters provide a comprehensive thermodynamic framework to represent all thermodynamic properties of aqueous electrolyte solutions including vapor pressure depression, mean ionic activity coefficients, osmotic coefficients, excess enthalpy, and heat capacity.
The DIPPR® 801 Database/DIADEM Software: Evaluated, Dynamic, and Simulator-Ready

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The DIPPR® 801 Database is a collection of thermo-physical property data with an emphasis on quality through a rigorous “systems-approach” evaluation procedure, currency by continually improving existing and adding new content, and completeness to ensure simulator-readiness.

Evaluated: DIPPR® 801 uses a systems approach in evaluating all available data for a given compound to triangulate on the best values and produce higher accuracy than could be achieved using only individual points. This approach includes hundreds of applied constraints such as inter-property relationships, expected smooth trends of properties between related chemicals, and the impact of chemical similarities and differences. Once these constraints are simultaneously satisfied for all properties, experts manually review and give final approval. Therefore, each compound in the database has evaluated, expert-recommended values for all properties.

Dynamic: New compounds and properties are added to the database each year, while improvements are made to data and correlations of existing compounds as new experimental data and prediction methods are discovered through an extensive frequent world-wide search of published and sponsor-donated data.

Simulator-Ready: DIPPR® 801’s vast collection of evaluated data is used to test and refine prediction methods such that when experimental data are not available, values for properties are predicted using prediction methods proven accurate for similar compounds. These predicted values are also subject to the same rigorous systems-level evaluation process mentioned previously. This eliminates “holes” such that accurate results are almost always achievable in simulation software packages.

The DIPPR® Interface and Data Evaluation Manager (DIADEM) is an interface and data analysis tool designed for use with the DIPPR® 801 database and with user-developed databases. Among other powerful features, DIADEM contains a 200-method property prediction package that enables users to obtain accurate estimated property values for any compound whether or not it is included in the DIPPR® 801 Database.
Saturated and Compressed Liquid Heat Capacity at Constant Volume for 1-Hexyl-3-methylimidazolium
bis(trifluoromethylsulfonyl)imide

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With the goal of developing a reference equation of state for ionic liquid (IL) 1-hexyl-3-methylimidazolium
bis(trifluoromethylsulfonyl) imide at conditions for one-phase liquid and for two-phase liquid + vapor equilibrium,
isochoric heat capacities ($C_v$) were reported for the first time [1]. The substance studied is often abbreviated
[C6mim][NTf2] and is the already well-studied IUPAC reference IL. Measurements were conducted over the
temperature range from (330 to 480) K and pressures up to 20 MPa using a high-temperature, high-pressure,
nearly constant-volume adiabatic calorimeter. As useful byproduct of the measurement, densities were reported
as a function of temperature and pressure. Measurements were made along liquid isochores in the range between
1218 kg⋅m^{-3} and 1279 kg⋅m^{-3}. Furthermore, measurements were concentrated near the liquid-gas phase transition
curve in order to closely observe phase changes. The values of temperature at the liquid-gas phase transition curve
for each measured isochore (phase transition parameters, $\rho_s$, $T_s$) were obtained by analysis of quasistatic
thermograms (readings of reference quality thermometer, $T-\tau$ plot, where $\tau$ is elapsed time) and barograms
(readings of pressure transducer, $P-\tau$ plot). The combined expanded uncertainties of the density, $\rho$, and isochoric
heat capacity, $C_v$, measurements at a 95 % confidence level with a coverage factor of $k = 2$ are estimated to be
0.06 % and 2.0 %, respectively. The combined expanded uncertainty of the phase-transition temperature is 0.02 K.
One-phase ($C'_{v1}$) and two-phase ($C'_{v2}$) liquid isochoric heat capacities at saturation and saturation liquid densities
($\rho'_s$) of IL ([C6mim][NTf2]) were measured. The measured values of saturated caloric ($C'_{v1}$, $C'_{v2}$) and saturated
thermal ($\rho_s$, $T_s$) properties were used to derive thermodynamic properties including ($C_p$, $C_v$, $W$, $K_T$, $\Delta H_{vap}$,
$(\partial P/\partial T)'_v$, and $(\partial V/\partial T)'_p$) of [C6mim][NTf2] at saturated liquid conditions. In addition, the second temperature
derivatives of the vapor pressure ($d^2P_s/dT^2$) and the chemical potential ($d^2\mu_s/dT^2$) at liquid + vapor conditions, and
the second temperature derivative of pressure at compressed liquid conditions ($d^2P/dT^2$)$_p$ were calculated directly
from the measured one- and two-phase isochoric heat capacity data. Values of ($d^2P_s/dT^2$) and ($d^2P/dT^2$)$_p$ derived
from calorimetric measurements were compared with the values calculated from vapor-pressure equations and
from an IUPAC reference equation of state for this substance.

References

Ionic liquids are salts entirely composed of ions, usually an organic cation and an organic or inorganic anion. The properties of these compounds can be manipulated by altering the nature and structure of the composing ions. Characteristics like hydrophobicity, biodegradation or toxicity can be taken into account when designing an ionic liquid to an industrial application. These unique properties of ionic liquids combined with the possibility of developing new and more efficient processes make them very attractive for industrial applications. The plethora of novel applications is expanding in areas such as electrochemistry, physical chemistry, analytics, engineering and biomedical industry, among others [1]. Although the number of publications in ionic liquids had grown tremendously, there are still quite unexplored themes. That is the case of the fluorinated ionic liquids family. This specific family of ionic liquids is characterized by having fluorine tags longer than four carbons [2]. Fluorinated ionic liquids are a viable option, with improved properties, in areas where perfluorocarbons find relevant applications, such as imaging agents, fluorocarbon gels, nanocompartmented supramolecular architectures and colloids, control and stabilization of emulsions, microbubbles and other colloids, pulmonary delivery of drug and genes and oxygen therapeutics. The presence of three nanosegregated domains (polar, nonpolar and fluorinated) in this specific family of ionic liquids was already proved [3]. In this work, we show how the balance between these three domains influences the thermal and thermophysical properties, namely density, viscosity, ionicity, conductivity and melting and decomposition temperature, of these compounds. The final aim of this study is to create knowledge that allows the design of fluorinated ionic liquid with desired properties for a specific application.

References

Phase Equilibrium and Density Measurement of Hydrogen and Carbon Dioxide Mixtures near the Supercritical Region at Pressures up to 12 MPa

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Thermodynamic properties of fluid mixtures containing hydrogen are of great importance in the coming hydrogen society. The transportation of hydrogen using natural gas pipelines is considered for instance, and the thermodynamic properties of hydrogen and hydrocarbons mixtures are required including the supercritical region. In addition, hydrogen is often used in reduction reaction, and characteristics of a variety of hydrogen mixtures are of much interest. Binary hydrogen systems with hydrocarbons and carbon dioxide show the divergence of the critical curves to a high pressure region, and the development of accurate equations of state representing the complicated behavior of the systems are desired. Hydrogen and carbon dioxide mixtures are easily in the supercritical state at moderate temperatures and pressures, and appropriate to be studied for understanding the complicated system having the critical curve divergence. Hence, an experimental apparatus available from -10 ºC to 50 ºC was developed to observe the phase equilibrium of hydrogen and carbon dioxide mixtures in this study, and the phase equilibrium has been observed near the supercritical region at pressures up to 12 MPa. Moreover, expansion vessels were installed to the apparatus, and the densities of the mixtures have been measured with the expansion method.
Potential of Semi-Clathrate Hydrates for Carbon Dioxide Capture

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Semi-clathrate hydrates (sc) are a type of clathrate hydrate in which the guest compound along with water molecules form the host framework and also occupy the cages of the structure. Quaternary ammonium/phosphonium salts such as tetra butyl ammonium bromide (TBAB), tetra butyl ammonium nitrate (TBANO₃) which form semi-clathrate hydrates have been extensively investigated for cold storage and secondary refrigeration applications. Recently, semi-clathrate hydrates have received attention as promoters for gas separation applications especially for CO₂ separation from fuel or flue gas mixture. In our recent kinetic works, we have identified several distinctive observations of these semi-clathrates applicable to CO₂ capture from pre-combustion streams. In this presentation, we will highlight the advantages and the drawbacks of using quaternary ammonium salts like TBAB and TBANO₃ for carbon dioxide capture based on kinetics of semi-clathrate hydrate formation varying the promoter concentrations and the operating conditions.
AFMIR is an analytical technique based on the photoacoustic effect: we optically monitor the deflection of the cantilever in a commercial AFM (Atomic Force Microscope) induced by a short pulse infrared (IR) laser, e.g. a QCL (quantum cascade laser), which is lightening the sample. The pulsed irradiation of an absorbing zone within the sample produces a fast local heating, which creates a thermal expansion of the heated zone and an acoustic wave propagating up to the sample surface where the AFM cantilever positioned. The detection of the transient deflection of the cantilever gives a signal corresponding to the surface deformation, i.e. related to the local infrared absorption. In this way chemical information of the sample can be recorded with spatial resolution levels in the sub-micron-regime. The investigated samples consist of an optically absorbing layer less than 100 nm thick on a thick transparent substrate coated with a polymer of several micrometers thickness (e.g. PMMA) or with biomaterials. For such thin absorbing layers the surface dislocation is not only determined by the acoustic wave but also by the thermal expansion of the heat diffusing outside the absorbing layer. Therefore thermal and acoustic equations have to be coupled to model the surface dislocations measured for several coatings of different thickness. This is in contrast to conventional photoacoustic imaging, where thermal confinement allows neglecting the thermal expansion outside the absorbing layer. The coupled model is used for depth profiling: from the measured cantilever signal the coating thickness, which is the depth of the absorbing layer, should be estimated. This is an ill-posed inverse problem for which Tikhonov regularization is used, and the resolution is determined as a function of depth. The actual resolution is compared to the principle resolution limit for AFMIR, determined by using the equality of information loss and entropy production.
Water and sodium chloride form a eutectic system. However, there are in literature only a limited amount of high-resolution thermal data on its phase behavior, although such information is quite relevant, e.g. for food engineering or cryobiology. We present high-resolution enthalpy and heat capacity data on sodium chloride solutions, ranging from pure water to the eutectic composition, in the temperature range between -30 °C to +10 °C. The measurements have been performed by means of a novel Peltier-element-based implementation of the adiabatic scanning calorimeter (ASC) concept [1,2]. The new instrument is capable of achieving, on mg size samples, accuracy (1 to 2 %) close to that of classical adiabatic heat-step calorimeters (on samples of several grams) and very high temperature resolution. ASC relies on the application of constant power to the sample, and measures the resulting temperature rate. This is exactly the opposite as in DSC, where a fixed temperature rate is enforced on the sample by varying the power. ASC leads naturally to high-resolution equilibrium data, in contrasts to inherently rate-dependent DSC data [3,4]. In addition, ASC also measures the enthalpy simultaneously with the heat capacity. We present specific heat capacity and enthalpy data for the melting of the ice and of the eutectic phase transition, around -21 °C. Accurate latent heat values are obtained for both transitions, as well as the melting point depression. A novel approach for purity determination on the basis of the data obtained by pASC will be discussed. These data will be used in a discussion of the colligative nature of the solutions and the dissociation of the salt.

References

Thermodynamics of the Lambda-Anomaly in Superconductivity

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At the transition temperature, $T_c$, of a superconductor there is a characteristic triangular line shape figure in the heat capacity versus temperature curve. This is often referred to as a lambda-anomaly. It is essentially the same for a wide range of classes and compositions of materials. This implies that the processes that contribute to, and are responsible for, the lambda-anomaly are independent of chemical composition. The anomaly is the result of the electronic fermion – boson wave function transitions that occur at, or near, the Fermi level energy, $E_F$. This is well known. What is not so well known, or is often overlooked, is the associated Fermi temperature, $T_F$. The Fermi temperature, that is $\sim 10^4$ K for some superconductors, is of prime importance in understanding the lambda-anomaly. By use of the concept of $T_F$ one can understand the difference of the signs of the chemical potential, $m$, for bosons and fermions. This also leads to estimates of the electronic enthalpy and entropy changes of some fermion – boson transitions at $T_c$. On the basis of the model considered the itinerant electron density in a fermion – boson transition is proportional to the height of the lambda-anomaly at $T_c$. 
The rheological behavior of heavy oils is critical for oil exploitation in different stages such as extraction, transportation and refinery. It is well known that viscosity of heavy oils is higher than light oils in several orders of magnitude. Temperature is a key parameter directly related with viscosity and non-Newtonian behavior of heavy oils. In particular, the viscoelasticity is a parameter that has not been extensively explored; however, it provides valuable information about the structure of the material. Heavy crude oils were characterized, the most of them with API gravity around 12. The measurements were carried out in a controlled stress rheometer with 40mm parallel plate geometry with a gap of 1 mm. The fluids were tested in rotational and oscillatory modes at temperatures from 5 to 100ºC. Fluids with similar API gravity were found to have zero shear viscosity very different, up to two orders of magnitude variation. This fact can be explained in terms of composition. The oils behave as shear thinning fluids for low temperatures and exhibit normal stress, which indicates the elastic component of the system. In the oscillatory experiments the magnitude of the loss and elastic modulus is presented. Above a critical temperature, the viscosity, the normal force and the elastic modulus decrease, suggesting that the non-Newtonian behavior is strongly related to the temperature. Furthermore, the departure from linearity in the curve zero shear viscosity vs temperature allows us to identify the change in rheological behavior from non-Newtonian to Newtonian fluid. The WLF equation was used in order to correlate viscosity with temperature, and was helpful to find the transition temperature.
Rheological behavior of heavy and light death oils have been studied. The oils belong to wells located in different regions of Mexico. The rheological measurements were carried out in a Stabinger viscometer and in a shear controlled rheometer with bob and cup and parallel plates geometry. The viscosity and rheological behavior exhibit a strong relation with temperature. For heavy oils, shear thinning was observed. The zero shear viscosity correlates with API gravity for the case of light oils. However, for heavy oils the viscosity definitively does not correlate the API gravity. For example, the viscosity of two fluids with API gravity around 12 varies in two orders of magnitude. An explanation of this finding may be due to the change in composition of the oil. Compositional structural analyses have been made for all oils in order to establish a correlation with viscosity. The transition between Newtonian and non-Newtonian behavior in terms of temperature has been studied, and it was found that non-Newtonian behavior does not directly relate to WAT.
Novel Experimental Methods to Quantify the Adsorption Thickness of Ionic Surfactant at Hydrophilic-Hydrophobic Interfaces

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In conventional energy production, the stability of liquid water or gas hydrate dispersions in the continuous hydrocarbon phase is determined by the energy bound at the hydrophilic-hydrophobic interface. Depending on the system’s chemistry, surfactants may be injected into the production system to manipulate or minimise this free energy and improve the ability of the system to flow. Conventionally, the performance of these surfactants is validated qualitatively through single-concentration interfacial tension or emulsion stability measurements. In this study, we used two experimental methods to quantify the competition between surfactants at hydrophilic-hydrophobic interfaces. First, pendant drop interfacial tensiometry (IFT) was adapted to quantify a matrix of adsorbed surfactant densities via Gibbs isotherm analysis. Ionic surfactants were studied over ten orders of magnitude in concentration. The results illustrate that ionic surfactants with similar molecular weight compete for adsorption sites at the water-oil interface, resulting in a decrease in overall packing efficiency below the critical micelle concentration. Second, Raman spectroscopy methods were adapted to quantify the extent of surfactant adsorption at the gas hydrate-oil interface above the dissolved concentration in the continuous phase. Together, these experimental methods can be used to develop structure-function maps for the development of future pipeline injection chemicals.
A Stethoscope-like 3ω Technique For On-Site Thermophysical Properties Measurement

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The 3ω measurement method is now widely used for thermal properties characterizations. The freestanding sensor based on polyimide film expands its application to much broader field, porous material, for example. Due to the existence of the polyimide film, the signal frequency must be low enough to ensure that it can penetrate the film and finally reach the sample. Lower frequency signal means larger time constant for the lock-in amplifier, thus the whole measurement process is time-consuming. In order to fundamentally reduce this time, new basement material for the freestanding sensor must be employed to increase the detection frequency and decrease the time constant. We choose sapphire as the basement for its high thermal diffusivity (more than one hundred times larger than the polyimide film), which is essential to determine the penetration frequency. Moreover, sapphire is rigid enough (which hardness is second only to diamond in nature) to resist most damage to the nickel strip deposited on it. A series of standard samples are tested by the new sensor, and results show that the stethoscope style freestanding 3ω technique make the measurement more rapid, and the sensor itself is more durable. Benefited from the reduction of measuring time, this technique achieves on-site measurement for the 3ω method, which means that thermal properties of most types of materials can be acquired easily, and the measurement process is no longer limited in laboratory.
Metals and metallic alloys often have high melting temperatures and highly reactive liquids. Processing reactive liquids in containers can result in significant contamination and limited undercooling. This is particularly true for molten silicon and its alloys. Silicon is commonly termed “the universal solvent”. The viscosity, surface tension, and density of several silicon-transition metal alloys were determined using the Electrostatic Levitator system at the Marshall Space Flight Center. The temperature dependence of the viscosity followed an Arrhenius dependence, and the surface tension followed a linear temperature dependence. The density of the melts, including the undercooled region, showed a linear behavior as well. Viscosity and surface tension values were obtained for several of the alloys in the undercooled region.

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Viscosity and Density Measurements of Water-Corexit 9500A-Alkane Organics

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The viscosity and density of selected binary and ternary mixtures of distilled water (or sea water)-Corexit 9500A-alkane mixtures were determined from 4°C to 40°C. The measurements were conducted at atmospheric pressure. Corexit 9500A is a commercial surfactant that was used extensively to mitigate the crude oil released during the Macondo well blowout. The concentration dependence of both the density and viscosity show nonlinear dependencies. At fixed concentrations the temperature dependence is linear, however, the functional dependence is unique to each concentration. Distilled water and sea water binary and ternary solutions have different behaviors and functional dependencies. Finally, the addition of linear alkanes to the sea water or distilled water system show different functional dependencies. In summary, for the current mixtures measured, in this study, we have not found any correlation from one concentration set to others.

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Implementation of Standards for the Reporting of Measurement Uncertainty for the Worldwide Thermodynamics Community

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In 2008, the Editorial Boards of the Journal of Chemical and Engineering Data, Fluid Phase Equilibria, The Journal of Chemical Thermodynamics, International Journal of Thermophysics, and Thermochimica Acta agreed to implement simultaneously a process for handling of manuscripts that, for the first time, allowed detailed checking and validation of experimental thermophysical and thermochemical property data in advance of publication. These procedures are centered at the NIST Thermodynamics Research Center, where thousands of articles are considered each year, with very large numbers of problems detected and resolved. A key aspect of this work has been the development and implementation of practical and effective reporting standards for the field that promote clear and complete data representations that are in accord with international standards for uncertainty assessment and representation (i.e., with the “GUM”). Successes and challenges in the implementation of uncertainty standards will be discussed within the context of the thousands of articles considered in the NIST-Journal cooperation, together with new tools and recommendations for further improvement.
The uranium dioxide is the most used oxide as nuclear fuel due to many advantages such as: high stability even when it is in contact with water in high temperatures, high fusion point, and high capacity to retain fission products. The conventional fuel for pressurized water reactors with UO$_2$ ceramic sintered pellets stacked inside fuel rods, and presents disadvantages because its low thermal conductivity causes large and dangerous temperature gradients. The research project entitled "Beryllium Project" under development at CDTN (Centro de Desenvolvimento da Tecnologia Nuclear/Comissão Nacional de Energia Nuclear, Belo Horizonte, Minas Gerais, Brazil) aims the obtaining of fuel pellets made from a mixture of uranium dioxide microspheres and beryllium oxide powder to increase the thermal conductivity of the fuel pellets. This type of fuel promises to be safer than current fuels, improving the performance of the reactor, in addition to last longer, resulting in great savings. Increase in the thermal conductivity in the range of 8.6% to 125%, depending on the level of addition employed in the range of 1% to 14% by weight of beryllium oxide, has been obtained. In this work, pellets with 2 weight percent of beryllium oxide were produced using the Nukem’s sol-gel process. The pelletizing parameters and the thermophysical properties (density, thermal diffusivity and thermal conductivity) results are reported and compared with the values of the conventional uranium dioxide nuclear fuel.
Group Contribution Model for Predicting Critical Volume with the Flory-Huggins Theory Asymptotic Behavior

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An assumption that has been made by the BYU DIPPR 801 staff in estimating property values for large molecules is that all families eventually converge to the n-alkane family with increasing chain length. For this purpose, much effort has gone into examining the n-alkane family. Specifically, the properties of n-alkanes as the carbon number approaches infinity have been studied to establish asymptotic convergence to other families. Since the critical point is an essential value for many predictive methods of thermophysical and transport properties, it is particularly important to the DIPPR 801 database. Historically, group contribution (GC) models for predicting the critical volume (VC) have assumed a constant contribution from each functional group. This assumption mathematically renders a critical density curve as a function of carbon number that monotonically increases until reaching a limiting value. However, in 1990 Teja reported an experimental maximum in critical density followed by a decrease for the n-alkane, 1-alkene, and 1-alcohol families. Siepmann verified this observed phenomenon by performing Gibbs Ensemble Monte Carlo simulations on large n-alkanes. With the findings of Teja and Siepmann, new prediction models needed to be developed. However, currently there exist two accepted models for predicting VC that have fundamentally different limiting behaviors that cause the correlations to diverge considerably around \( C_{20} \). This research focuses on simulating molecules large enough to determine the infinite carbon length behavior by performing rigorous nonlinear statistical analysis on a generic VC model. Having concluded which asymptotic trend is correct, a novel GC model was developed to agree with experimental data and the accepted trend. This new model reconciles traditional GC theory with Flory-Huggins polymer theory and provides flexibility when predicting small and large molecules of various families. Model validation is obtained by demonstrating how the new VC model improves liquid density prediction for large compounds.
Measurement of Surface Tension for Low GWP Refrigerants R1243zf, R1234ze(Z), and R1233zd(E)

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Low global warming potential (GWP) refrigerant R1243zf is a possible candidate to replace R134a for kitchen refrigerators and air conditioning applications. R1234ze(Z) and R1233zd(E) are very recently under consideration as the candidates to replace R245fa that is widely used in organic Rankine cycles and high-temperature industrial heat pumps. The capillary constant and surface tension of saturated R1243zf, R1234ze(Z), and R1233zd(E) were measured at temperatures from 274 K up to 350 K or the critical temperature, using a measuring apparatus based on the differential capillary rise method. The propagated uncertainty in the surface tension was typically 0.2 mN m⁻¹. The surface tension of R1243zf is approximately 0.5 mN m⁻¹ less than that of R134a at a temperature of 300 K, despite the R1243zf has a higher critical temperature than that of R134a. The surface tension of R1233zd(E) is more than 10% higher than that of R1234ze(E) at a given temperature. The experimentally quantified surface tensions were represented within 0.13 mNm⁻¹ by a van der Waals type equation expressing the temperature dependence as,

\[ s = 53.30 \left(1 - \frac{T_r}{T_{\text{crit}}} \right)^{1.247} \text{ for R1243zf} \]
\[ s = 56.57 \left(1 - \frac{T_r}{T_{\text{crit}}} \right)^{1.22} \text{ for R1234ze(Z)} \]
\[ s = 61.95 \left(1 - \frac{T_r}{T_{\text{crit}}} \right)^{1.277} \text{ for R1233zd(E)} \]

where, s and \( T_r \) are the surface tension and the reduced temperature, \( T_r = T / T_{\text{crit}} \). The critical temperatures \( T_{\text{crit}} \) are given as 376.93 K and 423.27 K for R1243zf and R1234ze(Z), respectively, by Higashi et al. (2014, 2013), and 438.75 K for R1233zd(E) by Hulse et al. (2012).
Nanoscale resolution imaging of cell metabolism is expected to visualize a single-cellular activity and to lead to an innovative drug development. However, the conventional method using an optical microscope cannot achieve a nano-scale resolution because of a diffraction-limit. This research is intended to reveal a metabolic activity on the surface of cells non-invasively using near-field fluorescence with high resolution. We have developed a novel local temperature measurement method using fluorescence near-field optics thermal nanoscopy (Fluor-NOTN). In order to achieve nanoscale spatial resolution, near-field light generated in the proximity of a small aperture was utilized. The sample surface-modified fluorophores are locally excited by near-field light, and fluorescence is detected by the small aperture. Fluorescence lifetime, which contains the information of the sample temperature, is then measured. In addition, an oxygen and ion concentration that are related to a cellular activity can be measured by a fluorescence lifetime sensing. In this report, a new scheme for fluorescence lifetime imaging system has been proposed in order to measure a temperature distribution of sample with nano-scale resolution. By controlling the probe-sample distance and the optical systems sequentially, the simultaneous detection of the fluorescence lifetime, fluorescence intensity and the topography of the sample can be achieved. Because the collected signal of fluorescence in near-field is extremely weak, a time correlated single photon counting method is utilized in order to gain a measurement sensitivity. Moreover, high-precision optical alignment system is proposed to suppress the optical noise. This system can improve the efficiency of collecting signal by automated alignment system that track a signal spot of fluorescence in near-field. Using our imaging system, we have visualized the cell adhesion and measure a distribution of fluorescence lifetime on the cell membrane.
The vertically aligned carbon nanotubes (VA-CNTs)/polymer composite is commonly fabricated by infiltrating the polymer in the space between CNTs. One of the main difficulties for the fabrication of VA-CNT/polymer composite is the efficient infiltration of polymer in the very narrow gap (50~300 nm) between the CNTs. In addition, the crust of entangled nanotubes on top of the VA-CNTs prevents the polymer infiltrating. It is necessary to develop the method infiltrating the polymer into the CNTs with keeping alignment of CNTs and pinholes-free. The present study describes the fabrication VA-CNT/polymer composite by depositing the parylene polymer by chemical vapor deposition (CVD). We have applied the photothermal radiometry (PTR) to measure the thermal conductivity of VA-CNTs/Parylene composite. In this method, a sample is heated by laser beam (wavelength 790 nm) modulated by a function generator operating from 1 Hz to 1 MHz. The temperature response on the sample surface is detected by the signal intensity change of infrared radiation. There is a phase-lag including the information of thermal properties between the signal and the modulated laser beam. By analyzing the phase-lag data using curve-fitting procedure derived from heat conduction equations, it is possible to determine thermal conductivity. We have fabricated VA-CNTs/Parylene composite under various conditions, e.g., type of parylene, thickness of VA-CNTs. From the cross-sectional view of the composite, we have found that infiltration of parylene into the VA-CNT was improved by depositing parylene from the substrate side. We have compared the measured thermal conductivity with theoretically estimated value.
The Fluoride Salt-cooled High Temperature Reactor (FHR) design employs fluoride salts to operate at high temperature and low pressure, which consequently leads to improved power conversion efficiency and safety of the nuclear reactor. This work is a critical review of the thermophysical properties of the fluoride salts of interest as FHR primary coolants. Discussed are the two coolants considered for a test reactor primary coolant—LiF-BeF₂ (flibe) with a 66-33 mol% composition and NaF-ZrF₄ with a 59.5-40.5 mol% composition. The thermophysical properties of these coolants are important for reactor design considerations, and when it comes to safety and licensing, quantifying the uncertainty of these properties is necessary. Unfortunately, experimental data is very limited, and most published properties do not report uncertainty. Additionally, almost every reported uncertainty is merely listed, which requires estimating its cause and how many standard deviations it covers. Recommended values or correlations and their corresponding uncertainty for the thermophysical properties of density (kg/m³), viscosity (Pa-s), thermal conductivity, and heat capacity are presented. For the primary coolants over the liquid temperature range, the coolants exhibit temperature independent heat capacity and thermal conductivity values of 2386 J/kg-K and 1.1 W/m-K respectively for flibe and 1172 J/kg-K and 0.49 W/m-K respectively for NaF-ZrF₄. Density temperature dependence is linear, and viscosity follows the Arrhenius equation. For flibe, the density correlation is 3413-0.4884*T[K] and viscosity is 1.16E-4*exp(3755/T[K]). For NaF-ZrF₄, density is 3829.7-0.889*T[K] and viscosity is 7.667E-5*exp(3977/T[K]). The uncertainties range from 2% for density to 20% for viscosity.
Reference Correlation of the Viscosity of Toluene from the Triple Point to 680 K and up to 500 MPa

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Toluene was the first reference liquid to be proposed (after water), as it is widely used as a basic compound for chemical synthesis and as an organic solvent. Furthermore, its unusually wide temperature range in the liquid phase (178 to 384 K) and its resistance to decomposition, makes it an ideal reference liquid for viscosity calibration purposes and apparatus validation. Thus in 2001, under the auspices of the International Association, a correlation for the viscosity of toluene as a function of temperature and density was proposed by Assael et al.[1]. The temperature range covered was from 213 to 373 K, and the pressure range from atmospheric up to 250 MPa. The standard deviation of the proposed correlation was 2.7\% (within a 95\% confidence limit). Following the publication of new low-temperature experimental data on the viscosity of liquid toluene along the saturation line, in 2006 a new correlation for the viscosity of toluene along the saturation line was published by Santos et al. [2]. Recommended values were proposed with uncertainties of 0.5\% (at the 95\% confidence level), for temperatures between 260 K to 370 K, and 2\% for 210 K to 260 K and 370 K to 400 K. Furthermore, the value of 554.2 ± 3.3 μPa s, was proposed for the viscosity of toluene at 298.15 K. In 2012 an equation of state for toluene was published by Lemmon and Span,[3] thus making possible the development of a wide range viscosity correlation for toluene. Hence, in this work, based on critically-assessed literature data, a new wide-ranging correlation for the viscosity of toluene, valid over gas, liquid, and supercritical states, is proposed.

References

Derived Measurement of the Enthalpy of Vaporization of Complex Fuels Using a Variable Pressure Distillation Curve Approach

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During the vaporization process of a fuel droplet, the composition is evolving as the fluid is being distilled. This results in transitioning thermo-physical and chemical properties of the fluid, which must be accounted for to accurately simulate the droplet regression and the combustion of the vapor phase. Typical vaporization models assume constant properties, primarily because of the lack of data available for complex fuels as a function of fluid distilled. One particular property of interest in describing the vaporization of a fluid is the enthalpy of vaporization. The enthalpy of vaporization is traditionally determined using calorimetry which does not lend itself as a viable technique to measure the evolving vaporization enthalpies of a distilling complex fluid. Alternatively, the Clausius-Clapeyron equation can be rewritten to provide an expression for the enthalpy of vaporization as a function of the fluid's vapor liquid equilibrium. To implement this strategy, the fluid's saturation temperature as a function of pressure must be measured. For a complex fluid, the saturation temperature as a function of fluid distilled can be determined using an improved distillation curve measurement technique. Using a variable pressure distillation apparatus in concert with thermodynamic principles, the continuous saturation temperature versus pressure is measured and used to evaluate the evolving enthalpy of vaporization as function of volume distilled for a complex fluid. This technique is applied to determine the varying enthalpy of vaporization of a diesel fuel and is validated by comparing values determined using a previously published compositional based technique. Initial data has demonstrated the potential of a variable pressure distillation curve approach to determine the evolving enthalpy of vaporization of a fuel as the fluid is distilled.
Wavelength-Modulated Differential Photoacoustic Spectroscopy (WM-DPAS) for Very Early Detection of Breast Cancer and StO₂ Quantification

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Biomedical photoacoustic (PA) imaging is a non-invasive imaging modality with unique hybrid optical-ultrasonic principles. Due to a number of advantages that PA enjoys over other biomedical imaging modalities, PA imaging has risen to the top of medical diagnostic procedures such as human breast cancer detection. While conventional PA imaging has been mainly carried out by a high-power pulsed laser, an alternative technology, the Frequency Domain Photoacoustic Radar (FD-PAR) is under intensive development at the Center for Advance Diffusion-wave Technologies (CADIFT). It utilizes a continuous wave optical source with the laser intensity modulated by a frequency-swept (chirped) waveform for acoustic wave generation. The small amplitude of the generated acoustic wave is significantly compensated by increasing the signal-to-noise ratio (SNR) by several orders of magnitude using pulse compression and matched-filter correlation processing in a way similar to radar systems. The current study introduces a novel FD-PAR modality for ultra-sensitive characterization of functional information for breast cancer imaging. The talk will introduce wavelength-modulated differential Photoacoustic spectroscopy (WM-DPAS) detection which has been developed to address angiogenesis and hypoxia monitoring, two well-known benchmarks of breast tumor formation. Based on the developed WM-DPAS theory, this modality efficiently suppresses background absorptions and is expected to detect very small changes in total hemoglobin concentration ($C_{Hb}$) and oxygenation levels ($StO₂$), therefore identifying pre-malignant tumors before they are anatomically apparent. The capability of the WM-DPAS to sensitively detect human breast pre-malignancy and quantify the corresponding breast carcinogenesis benchmarks was studied using an in-vitro blood circulation system. Comparison of the experimental results to the developed theoretical formalism will be presented and the clinical diagnostic prospects of WM-DPAS will be discussed.
Poly(2-hydroxyethyl methacrylate) (PHEMA), a synthetic crosslinked hydrogel, with outstanding ability to absorb and retain a high water content and still maintain their solid state, has been studied as scaffold for methane gas hydrates. The high water content, excellent hydrophilicity and interconnected pores of these hydrogels could be ideal to support the methane hydrate formation and to enhance gas permeation and interactions with water molecules. Supposedly, the heat released during the formation of 1 kg of methane hydrate is as much as 438.54±13.78 KJ. Whether the heat can be removed from the hydrate-hydrogel system in time is critical to the formation of methane gas hydrates, which is why high thermal conductivity, one of the thermophysical properties used to quantify the ability to conduct heat, is regarded as a favorable property. To better understand the thermal behavior of PHEMA hydrogel during the hydrate formation process, we investigate the thermal conductivity of PHEMA hydrogel under various temperatures ranging from 243 K to 293 K. Results were found that thermal conductivity is mainly influenced by 2 factors--ambient temperature and water content of hydrogel. At some point below 273 K, the thermal conductivity of all the hydrogels experiences a sudden rise to around 1.5 W/(m·K), about 3 times larger than before. We also found that the lower the water content is, the lower the transition point temperature will be. Additionally, we use TG and DSC together to investigate the water content and water state of hydrogels to better understand these hydrogels’ thermal behavior.
Poly(2-hydroxyethyl methacrylate) (PHEMA), a synthetic crosslinked hydrogel, with outstanding ability to absorb and retain a high water content and still maintain their solid state, has been studied as scaffold for methane gas hydrates. The high water content, excellent hydrophilicity and interconnected pores of these hydrogels could be ideal to support the methane hydrate formation and to enhance gas permeation and interactions with water molecules. The heat released during the formation of 1 kg of methane hydrate is as much as 438.54±13.78 kJ. Whether the heat can be removed from the hydrate-hydrogel system in time is critical to the formation of methane gas hydrates. In this work, thermal conductivity is investigated for different temperatures and monomer contents to better understand thermal behaviors of PHEMA hydrogel during the hydrate formation process. Several theoretical models were applied to calculate hydrogel’s thermal conductivity and the prediction results were compared with experimental values. Results were found that thermal conductivity strongly depends on monomer content and ambient temperature. With monomer content ranging from 100 wt% to 5 wt%, thermal conductivity can increase from 0.1259 W/(m·K) to 0.5907 W/(m·K). At some point below 273 K, the thermal conductivity of all hydrogel samples experiences a sudden rise to around 1.5 W/(m·K), about 200% larger. Other thermophysical properties like heat capacity and thermal stability were also investigated using differential scanning calorimetry and thermogravimetric analysis respectively.
Development of a High Pressure and High Shear Rate Capillary Rheometer for the Characterization of Extra-Heavy Oils

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At present oil still covers about 30% of global energy needs. Extra heavy oils represent almost 7% of this supply. Also in future, heavy crude oils will contribute as a relevant hydrocarbon source. Due to the declining oil reserves, an effective recovery of the available resources is becoming more important. Viscosity and flow behavior of heavy crude oils are key properties for the characterization, management and development of petroleum reservoirs. Under typical conditions, light petroleum fluids behave Newtonian while extra heavy oils tend to behave non-Newtonian. To measure the rheological properties of heavy crude oils with a high accuracy, a high pressure capillary rheometer has been designed and built. The experimental arrangement consists of two high-pressure vessels connected by a tube system and a calibrated capillary. Both vessels are equipped with a hydraulically operated metal bellow that can be varied in size by electrically driven spindle presses. By inflating one bellow and simultaneously shrinking the other one, the fluid is pressed through a capillary at a constant flow rate. The viscosity of the fluid is calculated from the volumetric rate of flow and the pressure drop with Hagen-Poiseuilles law solved for the viscosity. With the capillary rheometer, conditions up to 1000 bar and 200 °C can be generated. Viscosities between 0.5 and 80000 mPas can be measured under different shear rates. The capillary rheometer was calibrated with three Newtonian reference blends. For these standards the viscosity tables have been extended up to 1000 bar in the temperature range from 20 to 120 °C with a falling body viscometer. The capillary rheometer is then calibrated with the same reference fluids at the same conditions. Viscosity and flow behavior of different heavy crude oil samples are determined at reservoir conditions.
Non-Steroidal Anti-inflammatory Drugs (NSAIDs) are used to reduce the fever and to treat pain or inflammation caused by headache, toothache, back pain, arthritis, menstrual cramps or major injury. NSAIDs include sodium salicylate, sodium naproxen, sodium salt of meclofenamic acid and Sodium naproxen. Sodium naproxen reduces the chemical signals in our body that cause pain. Major solvent medium for the biochemical reactions that occur in our body is water. To understand the type and extent of physicochemical interactions between drug and water, thermodynamic, transport and acoustical properties are required. These thermophysical properties of aqueous solutions of sodium ibuprofen, sodium salicylate, and sodium salt of meclofenamic acid have been reported in earlier publications (1-3). This paper reports density, viscosity, ultrasonic velocity, conductivity, and refractive index data of sodium naproxen water solutions at (298.15, 303.15, 308.15, and 313.15) K. Density and conductivity data of sodium naproxen water solutions reported in the literature have been compared with new generated data. New data of density, viscosity, ultrasonic velocity, refractive, and conductivity are correlated with molality of the solutions. To get the information regarding the nature of sodium naproxen-water interaction, partial molar volume, isentropic compressibility, apparent molar isentropic compressibility, and limiting molar isentropic compressibility of sodium naproxen have been calculated.

Acknowledgement

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Thermophysical Properties of Aqueous Solutions of Sodium Naproxen

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Non-Steroidal Anti-inflammatory Drugs (NSAIDS) are used to reduce the fever and to treat pain or inflammation caused by headache, toothache, back pain, arthritis, menstrual cramps or major injury. NSAIDS include sodium salicylate, sodium naproxen, sodium salt of meclofenamic acid and Sodium naproxen. Sodium naproxen reduces the chemical signals in our body that cause pain. Major solvent medium for the biochemical reactions that occur in our body is water. To understand the type and extent of physicochemical interactions between drug and water, thermodynamic, transport and acoustical properties are required. These thermophysical properties of aqueous solutions of sodium ibuprofen, sodium salicylate, and sodium salt of meclofenamic acid have been reported in earlier publications. This paper reports density, viscosity, ultrasonic velocity, conductivity, and refractive index data of sodium naproxen water solutions at (298.15, 303.15, 308.15, and 313.15) K. Density and conductivity data of sodium naproxen water solutions reported in the literature have been compared with new generated data. New data of density, viscosity, ultrasonic velocity, refractive, and conductivity are correlated with molality of the solutions. To get the information regarding the nature of sodium naproxen-water interaction, partial molar volume, isentropic compressibility, apparent molar isentropic compressibility, and limiting molar isentropic compressibility of sodium naproxen have been calculated.
Online Data Resources in Chemical Engineering Education: Impact of the Uncertainty Concept for Thermophysical Properties

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In traditional chemical engineering education practice, students have relied on either handbooks or online resources for a thermophysical property value that is relevant to an assigned problem.[1] A property value consists of three parts, namely: the numerical value; its units of measurement; and, its uncertainty. Frequently, it’s this third part that is inadequately evaluated or is unknown in some cases. That can spell trouble, since uncertainty propagates through a problem’s solution to the result. We review the concept of uncertainty for thermophysical properties, its implementation in globally-adopted communication standards for properties data and the evolution of online data resources. To facilitate the translation of developments to engineering education, we employ NIST Web Thermo Tables to furnish properties data with their associated expanded uncertainties. We present pertinent examples for the engineering classroom [thermodynamics; fluid mechanics; heat and mass transfer] and an example application to research. These examples illustrate the practical combination of the concept of uncertainty with online data resources.

References

Nickel-based superalloy are gamma prime strengthened alloy with excellent mechanical and thermal properties at elevated temperatures as well as at cryogenic temperatures. The nickel-based alloys were improved to be resistant to creep and become stronger by changing the heat-treatment conditions. The applications of superalloy are in the aerospace, gas turbine, turbine blades for the jet engines, and automotive applications. The thermophysical properties of superalloy demand on thermal design. In this paper, the thermal diffusivity was measured using a laser flash method, and the specific heat capacity was measured using a differential scanning calorimeter (DSC). The thermal conductivity was calculated from the measured density, thermal diffusivity, and specific heat capacity. The thermal expansion was measured using a dilatometer. Measurement of thermophysical properties was performed within the range from room temperature, which is the temperature at which superalloys are commonly used, and 700 °C. This alloys are consist of various combinations of Ni, Fe, Co, and Cr, as well as lesser amounts of W, Mo, Ta, Nb, Ti, and Al.
Acid gases (mainly CO$_2$ and H$_2$S) are usually removed from gaseous streams by countercurrent contact with an aqueous amine solution. This is a consolidated industrial technology and is preferred to physical absorption because of the presence of the amine in the liquid phase, which undergoes to chemical reactions and so enhances the mass transfer. Due to the exothermicity of reactions, a temperature increase occurs in the absorber, affecting the equilibrium and the amount of absorbed acid gas, while in the regenerator the energy requirement at the reboiler strongly depends on the heat of desorption. A correct information on the enthalpy, then, is fundamental to design the acid gas removal section of an industrial plant, mainly in an energy saving perspective. The aim of the work is the analysis of the thermodynamics of the system composed of CO$_2$, water and MethylDiEthanolAmine (MDEA), a tertiary amine widely used also if a separate removal of H$_2$S and of CO$_2$ is desired. The study is focused on the computation of the heat of absorption, which, in the open literature, is a field less investigated than the one related to VLE calculations. It is related to the description of the Vapor-Liquid Equilibrium, performed with the Electrolyte-NRTL model, and thus of the adopted VLE parameters. New parameters have been obtained and checked against experimental data of VLE and of heat of absorption. They can be implemented in the commercial software ASPEN Plus$^\text{®}$ and employed for simulations of the amine scrubbing scheme.
Correlation for the Viscosity of Methane (CH₄) from the Triple Point to 625 K and Pressures to 1000 MPa

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A wide-ranging model for the viscosity surface of methane (CH₄) has been developed that incorporates the generalized friction theory (GFT). The approach requires, as the core thermodynamic model, a reference-quality equation of state (EoS). Here the EoS of U. Setzmann and W. Wagner has been selected for that purpose. All available experimental data, to the extent of our knowledge, were considered in the development of the model. The span of data used for the regression covers from the triple point to 625 K and up to 1000 MPa. The model reproduces most of the primary data close or within the reported uncertainty: under 0.3 % for temperatures between 200 K and 400 K and pressures up to 30 MPa and up to 2 % over the fluid surface to 200 MPa. For extended pressures the uncertainty increases to 5 % up to 500 MPa and to 10 % from 500 to 1000 MPa for the full temperature range. The best model performance is expected between 200 K and 500 K and pressures up to 200 MPa, where the uncertainty is expected to be between 0.1 % at low pressures and under 2 % at elevated pressures. The model extrapolates in a physically reasonable manner and may be used at pressures up to 1000 MPa and temperatures from the triple point to 1000 K.
Isobutanol (CAS NO: 78-83-1) and n-hexanol (CAS NO: 111-27-3) as a biofuel, which have been got more and more attention due to their high calorific value and combustion performance. The study of these compound present obvious industrial interest in engineering applications. New density data for isobutanol and n-hexanol over 9 isotherms \([283.15 \leq T \leq 363.15] \) K and 16 isobars \([0.1 \leq P \leq 100] \) MPa are reported. In this work, the experiment was conducted using a high-pressure vibrating tube densimeter system, which was calibrated with vacuum and water by the method of Lagourette et al. Moreover, R134a has been used as a reference fluid to validate the densimeter. A series of experimental data points have been measured in the framework of this work. The uncertainty of each obtained datum was estimated, and the maximum expanded uncertainty with a level of confidence of 0.95 \((k = 2)\) of density measurement for isobutanol and n-hexanol were 0.04% and 0.03%, respectively. The experimental density data were fitted with the Tait-like equation with an absolute average percentage deviation of 0.019% and 0.034% for isobutanol and n-hexanol, separately. In addition, these data were used to analyze the isothermal compressibility and the isobaric thermal expansivity for these fluids.
Thermal characterization of micro/nano-size fibers has been developed based on contact and non-contact methods, with one of the major drawbacks of contact methods being the uncertainty that is introduced by thermal contact resistance when fitting theoretical models to experimental data. Being non-contact, photothermal methods can eliminate this concern. In this work, the feasibility of photothermal fluorescence-based thermometry to determine the thermal diffusivity of thin fibers is investigated. The fluorescent spectra of CdSe ZnS core-shell quantum dots deposited onto a synthetic spider silk fiber were recorded at calibrated temperatures. An artificial neural network was trained based on different features of these calibrated spectra, with the intent on reproducing surface temperature oscillations of the fiber during sinusoidally modulated illumination by a laser. By means of the artificial neural network, both the absolute surface temperature and complex temperature variations were used to extract the thermal properties of the fiber from the axial distance and frequency dependence of the signal.
Liquid-crystal phases exist as intermediate phases between those of solid and liquid. The various different types of liquid-crystal phases may be characterized by varying degrees of molecular orientational and positional order. Molecules exhibiting such phases are anisotropic in shape, with rod-like or disk-like structures being the most common. The macroscopic structure of a liquid-crystalline fluid is strongly influenced by the collective behavior of its constituent molecules. Therefore, to study these fluids at a molecular scale is very important to further our understanding of the origin of larger-scale properties, such as chirality. Under certain conditions, rod-like molecules with chiral interactions can create large-scale twisted structures. These are called chiral liquid-crystal phases and have been the subject of a lot of recent attention. There are reports of various chiral structure types, e.g. the cholesteric phase ($N^*$), the smectic C$^*$ phase, the blue phase (BP I, BP II and BP III) and the twist grain boundary phase (TGB). However, to date, there is relatively little work focusing on the relationship between molecular chirality and these high-dimensional structures. In this research, Monte Carlo simulations were performed to investigate the phase transitions of chiral liquid-crystals. In order to describe chiral liquid-crystal molecules, we use the chiral Gay-Berne potential developed by R. Memmer[1].

References

Cage Occupancy of Hydrogen Molecules in the Structure I, II, H, and VI Hydrates

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Hydrogen (H2) is an interesting target as a guest molecule of clathrate hydrates, because H2 is enclathrated in the hydrate cages and simultaneously migrates relatively-freely through hydrate cages. In the structure II mixed hydrates with thermodynamic promoters, large-cage occupancy of H2 (so-called “tuning effect”) is possible by using a specific preparation method. For the tuning effect occurring, the competitive condition of H2 and promoter molecules toward the large-cage occupancy is required. There is no report on the tuning effect in the structures H and VI. In the structure I mixed hydrates with methane (CH4) or carbon dioxide (CO2) occupying both the small and large cages, Grim et al reported the competitive cage occupancy of H2 and CH4 (or CO2) in the small and large cages dependent on the compositions. In the case of a large structure I former not occupying the small cages, that is, under less competitive conditions, how is the large-cage occupancy of H2 in the structure I mixed hydrate? Is a specific method necessary? We will report the experimental results on the tuning effect in the structure I mixed hydrates. In addition, the cage occupancy of hydrogen molecules in the structure I, II, H, and VI hydrates will be summarized.
A new experimental setup is being developed at ITU for melting-point measurements on refractory nuclear materials at static pressures of up to 100 MPa. The goal is to limit the rate of sublimation and evaporation of materials with higher vapor pressures because the evolved vapor cloud may have adverse effects on the radiometric temperature measurement. Limiting the evaporation rate, as well as the experiment duration, is particularly important when investigating materials that tend to evaporate incongruently. This helps maintain the initial composition of the specimen. In addition, studying the pressure dependence of the melting point of nuclear fuels is relevant for their equation of state, as it provides important and rare data on the density of the liquid in the vicinity of melting. The technique is based on melting a specimen using a powerful continuous-wave Nd:YAG laser, typically in less than one second, and then reducing the laser power to allow the specimen to re-solidify while recording the thermogram. Interactions with the specimen holder are largely avoided by only melting a thin layer in the center of the specimen while keeping its periphery and rear side colder and solid (principle of the 'self-crucible' technique). The setup consists of a high-pressure vessel and associated gas-feed and compressor. Due to the radioactivity of the specimens, the high-pressure vessel must be enclosed in a glovebox, which is equipped with a suitable optical port. The vessel itself is fitted with a sapphire window. All opto-mechanical hardware is located outside the glovebox. The current status of the project will be reported, with a particular emphasis on the technical challenges and how they are being addressed.
An Ultrafast Multiple-Wire Microchip to Measure the Thermal Conductivity and Thermal Diffusivity of Gases

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Based on a silicon microchip, a miniaturized thermal transport-properties sensor was constructed. It allows the measurement of thermal conductivity and thermal diffusivity of less than 1 ml gas within a few milliseconds at a very low heating power. The microchip contains a 2000-μm-wide 300-μm-deep channel that is spanned by a series of thirteen unsupported bridges. These serve as one hot and twelve cold wires, acting respectively, as the heat source and the thermometers of the sensor. The cold wires are arranged symmetrically to the center hot wire at six different distances between ±50 μm and ±500 μm. To ensure high signal resolution, each thermometer is switched to its own Wheatstone-bridge circuit of the external IO-unit. The thermal conductivity is determined using the quasi-steady-state (QSS-) technique [1]. Here, a step pulse of a few milliseconds is applied to the hot wire while measuring the quasi-stationary response of selected pairs of thermometers. Their individual differences in temperature furnish the measurand on a redundant basis. The thermal diffusivity results from a time-of-flight measurement: a 100-μs-pulse is fed to the hot wire from where the resulting heat pulse propagates through the gas, in both ways passing one cold wire after the other. For each one of them, the arrival of the temperature maximum is detected. Again on a redundant basis, the thermal diffusivity is evaluated from all these points in time. A preliminary assessment reveals standard uncertainties for both measurands mentioned to be well below 5 %.

References

Dynamic Data Evaluation (DDE) appeared as an addition to thermodynamic research. It was designed to immediately update recommended values of thermophysical and thermochemical properties with the account of recent measurements. The experience of its use has shown that data evaluation generates a significant feedback so that it becomes an active part of the research process. That feedback may contain requests of clarification and additional information, revealed anomalies and inconsistencies. Several services powered by DDE are presently provided by NIST, covering experiment planning (ThermoPlan), literature search (ThermoLit), data access (ILThermo, Clathrate Hydrate Database, Web Thermo Tables), and revealing inconsistencies and anomalies (in-house ThermoData Engine checks in cooperation with major journals). However, the impact of DDE on thermophysical research needs to be and can be increased by wider involvement of the research community without increasing the complexity of the procedures. The existing and proposed self-services will be discussed and examples of the impact of DDE services on the quality of research reports will be shown. The aspects of availability, functionality, and ease of use will be considered. Recent contributions to the DDE technology will be represented and priorities of the future developments will be discussed.
This paper deals with experimental results for the speed of sound in liquid binary n-heptane+isoctane mixtures and the calculation of thermodynamic properties at temperatures from 298.15 to 523.15 K and at pressures up to 60 MPa. The speed of sound has been obtained using a method of direct time measurement of an impulse traveling through the investigated medium in the temperature range 298.15-523.15 and pressure 0.1-60 MPa and concentrations 0-100 %. The pressure was measured by dead weight gauge manometers. The temperature was measured by platinum-resistance thermometer. Mixture composition was prepared by a weight method and was kept under control by chromatography analysis before and after measurements. The error of the experimental data does not exceed 0.08 %.
The values of free energies, the heats and entropies of formation of atoms of I-VI groups of Mendeleev’s periodic table in gaseous and condensed phases were analyzed. Seventy nine equations of such type as \( \Delta_{c,f,s} Y^o = i \pm f N \), in which \( \Delta_{c,f,s} Y^o \) is thermodynamic function, \( i \) and \( f \) are stoichiometric coefficients. The obtained equations can be used for the calculations of the same functions for other atoms, for which they are not known. The same equations can be used for the next calculation of bond strength in them also. Instead of bond energy (\( E_b \)) or bond dissociation energy (BDE) the bond strength (\( S_b \)) new symbol of the bond powers for organic and organometallic substances has been suggested. It has been done because there are all thermodynamic functions for practically all atoms of Periodic table and hard to define the bond power with the use the heat function (enthalpy) only; probably is necessary to present all the thermodynamic parameters for the calculating bonds between atoms [1]. The heat of vaporization (\( \Delta_{vap} H^o \)), all thermodynamic functions \( \Delta_{c,f} G^o \), \( \Delta_{c,f} H^o \), \( S^o \), \( \Delta_{c} S^o_{\text{cond}} \) and heat capacity (\( C_p \)) of organic compounds of I-VII groups of Mendeleev’s Periodic table can be well characterized with the number of valence electrons \( N \) without taking into account the number \( (h) \) of lone electrons pairs \( (g) \) of them in equation \( \Delta_{vap,c,f,s} Y^o = i \pm f *(N - hg) \). The stoichiometric coefficients \( i \) and \( f \) reflect partially a various spatial structure of all investigated compounds. The free energy and entropy of combustion and formation are calculated only for oxygen, sulfur and partly fluorine compounds [2, 3].

References

New trends in the publication of thermophysical properties data for chemical substances are reviewed using, as an example, the properties of water and steam – the principal heat carriers and working bodies in thermal and nuclear power industries. The advantages and disadvantages of traditional publication on paper are examined in comparison with the modern electronic delivery via Internet. One important requirement for the latter is the inclusion of interactive calculations. Additional requirements for online calculation tools may include low or no cost to the users, multipy platforms (Windows, Android, Linux etc), multilingual interface (English, Russian, Chinese, German, Spanish, etc.), traditional math operators and functions, 2D and 3D graphic capabilities, animation, numerical and symbolic math, tools for solving equation systems (algebraic, differential, etc.), derivatives, integrals, as well as programming tools for setting conditions, local functions, etc. Using of computer animation for verification of functions for calculating thermophysical properties of substances is reviewed. An analysis of relevant Internet resources is given. Certain aspects of the work of the International Association for the Properties of Water and Steam (IAPWS) are described. New information technologies are described for publishing the data on thermophysical properties of substances using IAPWS formulations that can trace the errors in the code and optimize calculation process. Specific examples are provided of the development of modern IT resources for the modeling of the properties of chemical substances, including handbooks, desktop calculation software, downloadable online calculations, and calculations that use server technologies such as Mathcad Calculation Server (see the site of National Research University “Moscow Power Engineering Institute”) and SMath (see the site of Knovel, an Elsevier company). Keywords Thermophysical properties, working bodies, heat carriers, thermal energy generation, nuclear energy generation, thermal engineering calculations, Mathcad, SMath, Internet, IAPWS, Elsevier, Knovel
The similarity laws play important role in thermodynamics as far as they allow one to establish the general features of behavior for very different substances. The well-known examples of these regularities are the principle of corresponding states and the law of rectilinear diameter. For the liquid-gas domain of the phase diagram the van der Waals equation (vdW) serves as the most popular test model for the similarity laws. But it also can help to find new similarities. In particular, one more similarity, known as the Zeno line law (or simply Zeno-line - ZL), firstly was discovered as a consequence of vdW. This regularity concerns the states at the temperature-density plane, where the compressibility factor is unity. The curve containing the above states is appeared to be the straight line. It was shown that ZL regularity, characterized by $\rho_B$ and $T_B$ parameters, has a wide area of applicability than the other analogous regularities (see [1] and references therein). Besides this fact, ZL is the tangent to the liquid branch of binodal at T tends to zero. Recently we have found that one more consequence of vdW can also be generalized for other substance. This regularity concerns the enthalpy, saturation pressure, isobaric thermal expansion coefficient, Joule-Thomson inversion temperature. Namely for vdW the line where the enthalpy per particle coincides with the ideal gas enthalpy (H) is also the straight line (characterized by parameters $\rho_H$ and $T_H$). We have confirmed these regularities for the Lennard-Jones [2] system as well as for some other models and real substances.

References

In-Situ Measurements of Spectral Emissivities for Verification of MoSi2-Protective Layers on Metal Surfaces at High Temperatures

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Molybdenum disilicide (MoSi2) shows a good oxidation resistance by forming an amorphous SiO2 passivation film during heating in oxidizing atmosphere which prevents further diffusion of oxygen. This offers the possibility to produce coatings on metals surfaces by thermal spraying molybdenum disilicide as protective layer on construction parts in thermal plants exposed to oxidizing atmospheres at temperatures up to 1600 °C. Aim of the investigation was to find out if in-situ measurements of spectral emissivities could be an effective tool for the evaluation and verification of the layers. At first spectral emissivities of steel and molybdenum substrates without and with MoSi2-coatings were determined in protective atmospheres. Transmission of substrates radiation was not found, the layer showed a characteristic curve of temperature dependent spectral emissivities. The formation of MoSi2-protective layers depends on the heating parameters and does not lead to results which give an optimum oxidation resistance in any case. At about 400°C the so called pest-oxidation can occur which prevents the formation of the layer or leads to damages in existing layers. The investigations showed that differences between layers which are well-formed or influenced by these effects could be detected based on measurement of spectral emissivities. The temperature dependent formation of the layer in oxidizing atmosphere and the influence of pest-oxidation could be shown as strong changes of spectral emissivities at characteristic wavelengths or spectral ranges. In contrast to that, structural changes of the layer at the brittle-ductile transition at about 1000 °C have no influence. The investigations showed that temperature dependent in-situ measurements of spectral emissivities are an effective tool for the evaluation and verification of formation and long-term monitoring of MoSi2-based protective layers on metal surfaces. But it requires a measurement system that works quickly and over wide ranges of temperature and wavelengths.
Modelling of the Specimen Temperature Drop of a High Temperature Emissivity Measurement Facility

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Accurate emissivity measurement at high temperature, especially above 1000°C, plays a vital role in the high temperature processing, such as thermal modelling and radiation thermometry. However, it’s extremely difficult to achieve a satisfying result, and very few results were published before [M.Ballico, G.Neuer, G. Herdrich, M. Modest].

The key issue of accurately measuring high temperature emissivity is to maintain a hot surface without reflection of hot environment. We used the integral blackbody technique to solve such problem. A emissivity measurement apparatus at high temperature is building up based on this method at NIM. The apparatus consists of an air cylinder and a water-cooled copper cylindrical rod extension, it connects the air cylinder and a high strength graphite rod extending into a graphite tube furnace. Because of the reflections from the cylindrical section, the resulting cavity radiates as a blackbody. After the air cylinder rapidly moves the specimen to the end of the heater tube, the specimen exposes to the cooling environment. The ratio of the free standing radiation to the blackbody radiation is calculated, and it can be measured as the emissivity at high temperature[C. Liller].

In this study, the temperature drop of the specimen during the moving of the cylinder is simulated in order to achieve the accurate emissivity when the sample is exposed to the cooling environment. In this paper, a FEA model is used to model the thermal process and the results will be reported.
Microcalorimetric Measurement of a Physical-chemical Absorbent for CO2 Capture

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The traditional CO2 capture material, aqueous monoethanolamine (MEA), have a good CO2 solubility and a high absorption rate, but is expensive to regenerate in terms of energy cost and solvent loss. Instead of water, an aprotic polar solvent, diglyme, was used to dissolve MEA to form a physical-chemical absorbent MEA+diglyme in this work. To evaluate the performance of proposed absorbent, an experimental apparatus was designed and built up, which combined the microcalorimetry and the isothermal synthesis method. The apparatus was able to measure the CO2 solubility and absorption heat simultaneously. The calorimeter BT2.15, produced by SETARAM Instrumentation (Caluire, France), was used to measure the heat of CO2 absorbed by MEA+diglyme pre-stored in the vessel of calorimeter. The isothermal synthesis method has been used to measure solubilities of many vapor-liquid systems including CO2 in organic solvents, polymers, and ionic liquids. In this work, the isothermal synthesis method was used to measure the load of CO2 in absorbent corresponding to the absorption heat detected by the calorimeter. The CO2 solubility and heat of absorption in aqueous MEA were measured to validate the apparatus. Deviations between experimental data and data in literature were calculated, and the calculation indicated a good reliability of the apparatus. Then the CO2 solubility and heat of absorption in MEA+diglyme were measured. The obtained data were compared with that of aqueous MEA. Results indicated that both CO2 solubility and absorption heat in MEA+diglyme were less than those in aqueous MEA under CO2 pressures below ~1200 kPa and MEA concentration of 30 % (mass fraction).
Thin metal films are widely used as interconnecting wires and coatings in electronic devices and optical components. Reliable thermophysical properties of the films are required from the viewpoint of thermal management. The cross-plane thermal transport and phonon attenuation of two polycrystalline platinum nanofilms with different thickness deposited on glass substrates has been studied by applying the picosecond laser transient thermoreflectance technique. The measurement is performed by applying both front pump-front probe and rear pump-front probe configurations with high quality signal. The determined cross-plane thermal diffusivity of the Pt films greatly decreases compared to the corresponding bulk value, exhibiting significant size effect. The main mechanism responsible for the thermal diffusivity decrease of the present polycrystalline Pt nanofilms is the grain-boundary scattering on the free electrons.
A thermally assisted method for improving photoacoustic (PA) imaging depth and signal-to-noise (SNR) ratio is presented in this talk. Uniform heating, microwave and ultrasound localized heating have been studied as heating sources for imaging purposes. The temperature rise from microwave or ultrasound excitation was experimentally measured using thermocouples in ex-vivo beef muscle. The SAR (Specific Absorption Rate) distribution in the radial direction of the heated spot by microwaves or ultrasound was studied experimentally and theoretically. The measured temperature on the microwave heated surface spot or the center of a HIFU focal area was compared with theoretical estimates. The analytical method showed reasonable agreement with the measured results. The study also showed that microwaves can generate over three times higher temperatures than ultrasound in 30-s-heated beef muscle with the same input power.

The uniform-heating-assisted experimental results showed that the maximum imaging depth increased by 20% through raising the temperature of absorbing biotissues (ex-vivo beef muscle) uniformly from 37 to 43°C, and the SNR was increased by 8%. The microwave assisted localized heating (ex-vivo beef muscle) can increase the imaging depth by 11%, and SNR by 5%. The temperature dependence of the parameters comprising the Gruneisen constant (to which the PA signal is proportional) was investigated. The studies showed that the Gruneisen constant of biotissues increases with temperature. The thermal expansion coefficient contributes to the increase of Gruneisen constant more than other parameters.
Density Measurements on 0.95 CO$_2$ + 0.05 CH$_4$ at the Vicinity Of The Critical Point in the Supercritical State by Single Sinker Densimeter

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Measurements of volumetric properties of binary mixture 0.95 CO$_2$ + 0.05 CH$_4$ were performed at 300.15 – 313.15 K and 8.0 – 10.0 MPa, which is at the vicinity of the critical point in the supercritical state, with intervals 1.0 K and 0.2 MPa for temperature and pressure, respectively, by single sinker densimeter. The extended uncertainties (k=2) of measurement are estimated to be 21.5 mK for temperature, 3.39 kPa for pressure, and 0.024% for density. The combine density uncertainty is 0.039% - 0.026% in 11 – 31 MPa. The uncertainty contribution from molar fraction to density is possibly up to 0.115%, with mixture preparation and gas absorption and desorption effect as the domination factors. The measurement results were compared with GERG-2004 equation of state. Generally, the deviation from experiment data to GERG-2004 EOS increases when approaching to the critical point, peaking at -4.8% at (301.07K, 7.97 MPa). In an isothermal state with increasing pressure, the deviation reaches maximum when crossing the Widom Line. The isobaric expansibility $\alpha_p$, i.e. $(\partial V/\partial T)_p$, was calculated from the experiment results and a maximal locus of $\alpha_p$ in the measuring range is obviously observed. The maximal locus stretches close to critical point but the critical point is not on the extension of this maximal locus. This phenomenon is different with that in purity, for which critical point is on the extension of the maximal locus of $\alpha_p$. 
The thermal conductivity of insulating material is measured over a temperature range of 10 K to the approximately room temperature. A two-stage cryocooler is employed as a heat sink to cool the test specimen down to a desired temperature. In a vacuum vessel, the cold heads of the cryocooler are thermally connected to the specimen as well as the thermal shield. An electric heater is placed in the middle of the test specimen for generating uniform heat flux. For a supplied heat flux the temperature distribution in test specimen, multi-layer insulation (MLI), is measured in steady state, from which the effective thermal conductivity is calculated and presented with respect to the mean temperature. The correlation at temperature between liquid nitrogen and room temperature is derived from measured data. In addition, the effect of the contact pressure, operating temperature and type of material on the thermal conductivity are investigated.
Laser Flash Raman Spectroscopy Method for Thermophysical Characterization of Nanomaterials

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Recently, a noncontact technique based on the temperature dependent Raman band shift has been applied for thermophysical characterization of low dimensional nanomaterials. However, in most measurements the laser absorptivity requires to be determined beforehand and the difficulty of accurately determining the laser absorptivity significantly limits the accuracy of this Raman technique. In general, to avoid the direct measurement of the laser absorptivity, a direct current is supplied to eliminate the laser absorptivity in theory, making the experiment more difficult and samples at a risk of burnout. To solve these problems, in this work, a transient “laser flash Raman spectroscopy” method is presented to characterize the thermal properties of low dimensional nanomaterials, with which the laser absorptivity can be easily eliminated and the electricity is needless. The measuring method for the thermal diffusivity and thermal conductivity of individual micro/nano wires is first presented. In this method, a focused short pulsed laser and a continuous-wave (CW) laser in a Raman spectroscopy system are served as a local heater, Raman signal excitation source and also a temperature sensor. Transient and steady-state heat conduction models are established to obtain two independent equations for the thermal diffusivity and laser absorptivity. This new method has been verified by comparing experimental results of a graphite carbon fiber with measurements employing the 3ω method. Further, the method is used to measure the temperature dependent thermal diffusivity and thermal conductivity of individual carbon nanotubes (CNTs), which fit well with theoretical trends. The present transient method has further been extended to 2D nanomaterials. By using a transient heat conduction model in cylindrical coordinate, the thermophysical properties can be determined by fitting the curves of the normalized temperature rise versus the laser pulse width for various laser spot radii. The uncertainty caused by temperature measurement is analyzed theoretically and through a case analysis of silicon nanofilm, changing laser spot radii is proved to be more easily in practical use than changing laser pulse width.
One of the most important subjects in thermodynamic property research field is to determine the universal gas constant, $R$, or the Boltzmann constant, $k$, to contribute to the re-definition of the thermodynamic temperature. The most promising experimental approach is speed-of-sound measurement for gas, so called acoustic gas thermometry (AGT). Recent progress in AGT techniques remarks the relative uncertainty for the universal gas constant being less than 1 ppm. On the other hand, other experimental techniques such as dielectric constant gas thermometry (DCGT), Johnson noise thermometry (JNT), or Doppler broadening thermometry (DBT) are competitive for the moment. In this study, therefore, a completely different approach to determine the universal gas constant was proposed. Namely, the universal gas constant is determined from gas-phase PVT property measurements. Since density calibration techniques for solid sample are well established recently, it is possible to improve measurement performance in gas density measurements to ppm level. In the present study, apparatus for gas-density measurement using a hydrostatic weighing of 1 kg silicon sphere was designed. By measuring buoyancy force acting on the sphere, gas density can be measured with an uncertainty around 1 ppm. The gas pressure is measured by a dead weight piston-cylinder balance which is calibrated against the national pressure standard in NMIJ. The apparatus is thermostated at 273.15 K within a good temperature stability less than 0.1 mK. The present status of this study, estimated measurement uncertainties, gas samples considered is presented.
Density and Viscosity Measurement of Biodiesel Fuel by Using a Vibrating-Tube Densimeter and a Capillary Viscometer

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Density and viscosity of biodiesel fuel were accurately measured by using a vibrating-tube densimeter and a capillary viscometer. These thermophysical properties of biofuels are necessary not only to domestically and internationally trade, but also to control their qualities as fuels in practical use. A commercially available vibrating-tube densimeter (DMA5000, AntonPaar GmbH) was used for the density measurement. Biofuel samples are generally easy to change their physical and chemical properties in atmosphere due to their high hygroscopicity and oxidizability. To prevent these effects on the density measurement, the densimeter was placed in a glove box whose inner ambience was controlled with low humidity and oxygen concentration. Mechanical constants of the vibrating-tube were calibrated with density standard liquids in a manner traceable to SI units, and thermometers installed in the densimeter were calibrated on the basis of ITS-90. Viscosity effect on the density measurement was taken into account by calibrating with three density standard liquids whose viscosities are different one another. An expanded uncertainty ($k = 2$) of the density measurement is estimated to be 0.06 kg m$^{-3}$ at room temperature.

Measurement results for biodiesel reference materials by NIST, SRM2772 and SRM2773, show that the measured densities agreed well with the certified densities of the reference materials within the measurement uncertainties. A glass capillary viscometer, whose apparatus constant was calibrated on the basis of viscosity of water, was used for the viscosity measurement. An expanded uncertainty of the viscosity measurement is estimated to be 0.06 %. A certified reference material (CRM) of biodiesel produced from palm oil is now under development at NMIJ/AIST. Some results for the density and viscosity evaluation of the biodiesel CRM will be presented.
Localized Wrinkling of Thin Films on Shape Memory Polymer Substrate

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Shape memory polymers (SMPs) can remember different shapes and can recover to their permanent shapes from temporary shapes with appropriate stimuli, such as heat, humidity, and electrical field. Using pre-programmed heat responsive SMP as substrate, we demonstrate a self-assembly fabrication method for programmable localized surface wrinkling. Different from global wrinkling in most of the literature, locally heating the thin film-substrate system causes localized recovery in the SMP substrate and thus induces localized thin film wrinkling. The wrinkle pattern shows good sinusoidal profile, with wavelength and amplitude decreasing gradually with the distance from the heating source. The surface wrinkle area can also be tuned by controlling heat input. In addition, the spectrum test was also performed, which shows peak shift of the spectrum with location due to wavelength change. This study can offer a simple and programmable method to fabricate localized wrinkling pattern, with potential applications in programmable optical gratings, surface property control, and other demanding applications.
Nowadays, some synthetic polymers have been replaced by biodegradable polymers in order to avoid environmental contamination. Among these biodegradable polymers, aliphatic polyesters like Polylactic Acid (PLA) and Polycaprolactone (PCL) have been widely used. In the present study solvent casting films of PLA, PCL and polymer blends with and without compatibilizer (PLA grafted with maleic anhydride) were prepared. The thermal diffusivity ($\alpha$) of each sample was obtained by using the open photoacoustic cell (OPC) technique. Morphology, degree of crystallinity and thermal properties were determined by using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD) and Differential Scanning Calorimetry (DSC), respectively. The PLA/PLA-g-MA/PCL (80/10/10) blend was more homogeneous and better adhesion between the two polymers was observed. The degree of crystallinity was similar for the blends without compatibilizer, being higher for the compatibilized blend. The PLA/PLA-g-MA/PCL (80/10/10) blend showed cold crystallization with the highest value of enthalpy of fusion ($\Delta H_m$) and the highest value of thermal diffusivity ($\alpha$). PLA-g-MA as compatibilizer enhanced thermal properties like thermal diffusivity which was increased due to more interactions between polymeric phases (PLA and PCL) was improved. To our knowledge this is the first time that the thermal diffusivity of these biodegradable polymer blends is reported.
The Study of Thermal Diffusivity Measurement Based on Frequency Scan Photothermal Reflectance Technique

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A frequency scan photothermal reflectance technique to measure thermal diffusivity of bulk samples is studied. Similar to general photothermal reflectance methods, an intensity-modulated heating laser and a constant intensity probe laser are used to determine the surface temperature response under sinusoidal heating. The approach involves fixing the distance between the heating and probe laser spots, recording the phase lag of reflected probe laser intensity with respect to the heating laser frequency modulation, and extracting thermal diffusivity using the phase lag – (frequency)^{1/2} relation. The measurement recipe is given with the discussion of deciding the proper measurement frequency range and the distance between laser spots. The experimental validation is performed on three samples (SiO₂, CaF₂ and Ge), which have a wide range of thermal diffusivity. The measurement results agree well to thermal diffusivity values reported in the literature. Comparing to the commonly used spatial scan photothermal reflectance method, the experimental setup and operation of the frequency scan method are simplified, and the uncertainty level is equal to or smaller than that of the spatial scan method. It is also found that the frequency scan method works particularly well on measuring the thermal diffusivity of the substrate material with a thin film coating.
Electrocaloric effect (ECE) has been known for many decades, however, the relatively small ECE observed
Promoted Electron Transport and Sustained Phonon Transport by DNA down to 10 K

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This work reports on a pioneering study of the electron transport in nanometer-thick Ir film supported by a DNA fiber, and the phonon transport sustained by the DNA itself. By evaluating the electrical resistivity ($\rho_e$)-temperature relation based on the Block-Grüneisen theory, we find the Ir film has weak phonon softening indicated by 7~15% Debye temperature reduction. The Ir film’s intrinsic $\rho_e$ is promoted by DNA electron thermal hopping and quantum tunneling, and is identical to that of bulk Ir. Although the nanocrystalline structure in ultrathin metallic films intends to give a higher Lorenz number since it reduces the electrical conductivity more than thermal conductivity, the DNA-promoted electron transport in the Ir film preserves a Lorenz number close to that of bulk crystalline Ir. By defining a new physical parameter entitled “thermal reffusivity”, the residual phonon thermal resistivity of DNA is identified and evaluated for the first time. The thermal reffusivity concept can be widely used to predict the phonon thermal transport potential of defect-free materials. We predict that the thermal diffusivity of defect-free DNA fiber could be 36~61% higher than the samples studied herein. The structure domain size for phonon diffusion/scattering is determined as 0.8 nm in DNA.
The mainly on using HCFCs (hydrochlorofluorocarbons) refrigerants and their traditional substitutes (such as R410A, R407C etc.) are not environmentally friendly, since which possess the slighter ozone depletion potential (ODP) and larger global warming potential (GWP). As one of the candidates of the new generation refrigerants, HFO-1234ze (E) possesses the suitable thermodynamic properties and small climate change effects. Researchers have been studied the possibility of using HFO-1234ze (E) as a refrigerant in chiller. However its flammability have not been detected completely. This paper contributed to the fundamental flammable characteristics and influence mechanism of HFO-1234ze (E) as well as its blends mixed with refrigerant HFC-161 (fluoroethane) theoretically and experimentally. Firstly, the flames were investigated under various testing conditions. And then the influences of humidity of air and the lubricating oil on the flammability limits of HFO-1234ze (E) were tested and analyzed. The results indicated that the water vapor played a obviously impact on the flammability of HFO-1234ze (E), leading to the flammability ranges of about 7.4% in volumetric concentration. As for the lubricating oil, the influence on flammable characteristic of HFO-1234ze (E) depended on the mixing conditions. Thirdly, both the lower flammability limits (LFLs) and upper flammability limits (UFLs) of HFO-1234ze (E)/HFC-161 were tested under ten different concentration ratios. The results showed that HFO-1234ze (E) possessed a slight flame suppression effect on HFC-161 but could not make it unburnt completely under the experimental conditions.
We present the first study on the simultaneous capillary instability among concentric viscous toroids. An array of concentric polystyrene (PS) toroids were lithographically fabricated with a constant radial spacing between neighboring toroids. The toroids were confined in a poly (methyl methacrylate) (PMMA) matrix. PS and PMMA were used because of their immiscibility and well-characterized physical properties. The glass transition temperature ($T_g$) of the pattern are well above room temperature. We found that the radial contraction mode of toroids (Pairam & Fernández-Nieves, PRL 2009) was inhibited due to substrate confinement and high viscosity of the medium. We identified three regimes of correlation depending on the degree of substrate confinement. When the degree of confinement was negligible and the toroids were spaced relatively far apart, the breakup behavior among toroids was non-correlated. By decreasing the relative spacing between toroids, the breakup became correlated. When the toroids were strongly confined, the breakup behavior of the toroids became in-phase correlated in the radial direction. In this case, geometric frustration due to the toroidal curvature was observed, which led to an intriguing branching behavior in the correlated instability and closely resembles a Cayley tree with fractal coordination number of 3.
Coating materials that can maintain the desired color in the visible range while reflecting near-infrared radiation from the sun are highly demanded for energy efficiency buildings or vehicle exterior coatings. Over a number of years, INCA has developed surface treatment technologies (e.g., solar off-loading technology) that provide the effect of insulation for building and industrial applications and outperform some of the most popular infrared reflective paints containing mainly titanium dioxide pigments. Field tests under solar irradiation or lamp irradiation suggest that the temperature rise can be reduced by 3-8°C compared with uncoated fabric of the same color. This is accomplished through color matching in the visible range, near-infrared reflecting, and high thermal emission in the long wave region. In this study, the spectral optical and radiative properties of coated and uncoated fabrics are measured using a monochromator (wavelengths from 400 to 1800 nm) and a Fourier-transform infrared spectrometer (wavelengths from 1.5 to 15 μm), coupled with white reflecting and gold reflecting integrating spheres, respectively. The results are to be used in a thermal analysis to interpret the outdoor thermal test results. This study will be important for the development and application of thermal management and energy saving coatings for exterior walls or fabric surfaces.
Several aspects of nanoscience and nanotechnology involve the use of liquids in contact with nanomaterials, for example as solvents for the dispersion, preparation and chemical modification of nano-objects, as media for transport through nanopores, or as electrolytes in energy-storage devices. In order to understand and control matter at the nanometer level we have to understand the properties of the fluid media, which do not behave as a simple continuum at these scales, and of the interfaces. We must describe in detail the molecular interactions between the fluids and the nanomaterials, an area where important progress can been made. This presentation will focus on ionic liquids as media to dissolve different kinds of nanoscale objects. Ionic liquids interact through Coulomb and van der Waals forces (including hydrogen bonds), and form organized phases that are heterogeneous at the nanometer scale. Among the nanomaterials of interest are 2D-layered solids in which covalently bonded sheets with thickness of one or a few atoms are held together by van der Waals forces. Examples are functionalized graphene, hexagonal boron nitride or molybdenum disulfide. In these materials the inter-layer forces are of a similar nature as those present in liquids. Some of the challenges these systems pose, mainly to the field of molecular simulation, are: i) the heterogeneous structure of the ionic liquids matches the size of the nano-objects leading to solvation effects that are not present in simple molecular liquids; ii) most often different classes of atomistic model are used to represent the liquid phase and the materials, and so the fluid-solid interactions necessary for molecular simulation studies are not sufficiently well known; iii) the functionalization of the materials drastically changes their interactions and affinity for different solvents; iv) dissolution and exfoliation are phenomena that happen on longer time scales than what is possible to simulate at the atomistic level, nonetheless it is important to describe interactions in detail. The final aim of this study is to improve our understanding of the physical chemistry of systems containing liquids and nanomaterials, enabling the rational design of solvent systems.
Properties of Saline Solutions for Process Design using Padé Approximants and Artificial Neural Networks

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Padé approximants are used to model physicochemical, transport and thermodynamic properties of seawater for industrial applications. Padé approximants are rational functions in which the numerator is a polynomial and the denominator is another polynomial, \( Q_m(x)/R_n(x) \). As known, water scarcity is one of the main challenging problems in industry and is of especial relevance in mineral processes in which water consumption is huge and also because mining operations are usually located where there is no water or water is extremely scarce. The main problem in using seawater in industry is the salt content certainly affects the properties of the water and the processes in which such water is used. Sophisticated mathematical models to calculate saline solution properties, such as high degree polynomials, potential functions or logarithmic expressions, have been presented in the literature for applications in which very high accuracy is needed. Models for estimating properties for industrial processes have received less attention. The properties studied are density, specific heat, osmotic coefficient, viscosity, thermal conductivity, surface tension, enthalpy, entropy, vapor pressure, latent heat of vaporization, and boiling temperature elevation. After analyzing the models available in the literature for the properties of seawater and observing the form of the curves at several temperatures and salinities, it seems that sophisticated mathematical models are not necessary for industrial applications. Padé-type model considering the variables temperature and salinity have been considered and analyzed in this paper. The general Padé model resulted to be accurate enough to represent all properties and give deviations similar to those provided by more sophisticated models presented in the literature and similar to Artificial Neural Networks also calculated by the authors. The advantages of these different models, sophisticated mathematical models, Artificial Neural Networks and Padé approximants, are also discussed. Computer codes and spreadsheet for determining seawater properties are provided.
Commercial imaging systems such as computed tomography and magnetic resonance imaging are frequently employed for observing living structures. However, they cannot visualize several tens of micron sized structures deep within the body. We describe a combined photoacoustic radar (PAR) and ultrasound (US) imaging system which was used to image blood vessel phantoms with high resolution based on the optical contrast and the anatomical details using gold enhanced contrast agents. The optimal optical power modulation power spectral density (PSD) was determined in the range of 0.5-0.8 MHz and 0.3-1.0 MHz for USI and PARI, respectively with the PAR amplitude of lower concentrations being higher than that of higher concentration samples. USI produced a better structural image of the tubing containing Au only and PARI produced a better functional image of the blood vessel. 2-D images of the blood vessel phantom were obtained. It is hypothesized that the change of the opto-thermal properties of higher gold concentration possibly decreases the osmolarity due to temperature increase and hence caused thermo-haemolysis of red blood cells (RBCs) which degraded the photoacoustic signal and thus the imaging contrast compared with the lower concentration.
The Dependencies of Lattice Properties Versus of Size and Shape for the Nanocrystals of Diamond, Silicon and Germanium

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A model of nanocrystal in the form of a rectangular parallelepiped with a variable surface shape (RP-model) is used to study of the dependencies of the modulus of elasticity, Poisson's ratio, Young's modulus, shear modulus, coefficient of thermal expansion and heat capacity versus of size and shape of the free-standing nanocrystal of the simple matter. The concrete calculations are done for diamond, silicon and germanium. It is shown that at the isomorphous decrease of size for nanocrystals of diamond, Si or Ge the values: modulus of elasticity, Young's modulus, and shear modulus are decreasing, but functions: Poisson's ratio, coefficient of thermal expansion, and heat capacity are increasing along isotherm. Than nanocrystal shape deviates from the most energetically stable shape (for RP-model it is cube), the more noticeably the changes of mentioned functions at the decrease of the nanocrystal size along of isotherm. The calculations for the nanocrystal of silicon have shown that at the isomorphous reduction of size along isotherm of 100 K the coefficient of thermal expansion at defined size passes from the negative into the positive field.
According to the Rosencwaig and Gersho theory for the photoacoustic effect (PA) in solids, the thermal diffusivity of human enamel and dentin was determined. The Rosencwaig and Gersho model describes the PA effect in a sample inside a hermetically sealed cell (photoacoustic chamber), in which the incident modulated radiation absorbed by the sample generates thermal waves. These waves in turn generate pressure variations in the gas content in the chamber, which can be detected by a microphone and transformed into an electrical signal which is amplified and stored for later analysis. The results indicate that the crystallinity and porosity in the enamel and dentin are important factors influencing the heat diffusion through the different structures of dental enamel and dentin.

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The applications and importance of prediction of solubility of organic molecules spans across a large sector of the chemical and pharmaceutical industries. The diverse and wide range of molecules for which such predictions are needed also have a wide range of other physicochemical properties.. A successful method to predict solubility of solutes in solvents for such a variety of compounds needs to be very versatile in terms of the types of molecules it can describe, while being accurate over broad ranges of conditions. Group contribution approaches can be very powerful techniques in this context. In the SAFT-$\gamma$ Mie group-contribution approach [1] a heteronuclear model is implemented and an accurate expression for the Helmholtz free energy change due to association is obtained for pure components. The physicochemical properties of molecules of interest are described by appropriate summation of the contributions of the groups they contain. Each of the groups is characterised based on the fluid phase behaviour and properties of simple molecules, and the parameters characterizing the groups are then transferred to more-complex molecules. The robustness of the underlying physics allows the treatment of a broad collection of compounds, including associating ones, and provides the ability to describe a wide array of physicochemical properties with a single set of interactions. Although the group-contribution method enables many molecules to be treated with a small number of constituting groups, the power of the approach is truly demonstrated when the solubility of large and complex multifunctional pharmaceutical molecules is predicted based only on experimental data that were obtained for small and simple molecules. Here we provide a wide range of examples of the prediction of solubility of organic molecules ranging from asymmetric alkanes mixtures to lovastatin in various solvents.

References

Estimation of Multicomponent Interfacial Density Profiles from a Direct Minimization of the Free Energy Surface

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The application of the gradient theory for the estimation of surface tension has recently acquired a renewed interest, particularly for multicomponent mixtures. The application of the gradient theory for the estimation of the surface tension of mixtures is perhaps the most powerful and straightforward method, provided the interface density profiles are known or can be estimated in a robust manner. It is precisely in the estimation of the density profiles, and the associated influence parameters, where the application of the method may run into several shortcomings that are not always easy to overcome, such as numerical convergence. In this work, an alternative theory is presented which allows for the accurate calculation the interfacial density profiles directly from the Helmholtz free energy surface, greatly simplifying the application of the gradient theory to just about all type of fluid mixtures. The theory presented in this work has also been confirmed by molecular simulation (MS) results. The analysis between the MS results and the theory is also presented and discussed in this work.
Time Domain Differential Raman for Thermal Diffusivity Measurement

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Raman scattering is not only applicable for structural characterization of molecular configuration and conformation in chemistry, but also relevant to physical properties of materials, such as temperature and stress. Thus information about temperature of specimen can be evaluated from intensity, Raman shift and linewidth of Raman signals. This provides the theoretical foundation for characterizing temperature by Raman scattering. In this work, a brand-new time-domain differential Raman (TD Raman) technology is developed to measure the thermal diffusivity of materials. The TD Raman technology uses a variable pulsed laser to heat the specimen and probe the temperature variation based on the principle of Raman thermometry and transient electrothermal (TET) technique. To evaluate this technique, silicon tipless cantilevers are used to conduct the experiment. A silicon tipless cantilever is heated by laser pulses and then Raman scattering spectrum of the specimen is collected. First of all, we develop a physical model to relate the accumulated Raman signal to the instantaneous Raman emission with temperature-dependent intensity, Raman shift, and linewidth. Then we develop a physical model to determine the thermal diffusivity of the cantilever by fitting curves of normalized Intensity and Raman shift against time. Sound agreement is obtained between the measured thermal diffusivity and the reference value. The TD Raman technology provides a very promising noncontact technique to measure the thermal diffusivity of materials without need of the temperature coefficients of Raman signals.
Instrumental Advances in the PLOT-Cryoadsorption Method of Vapor Characterization

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The use of purge and trap methods for sampling volatile organic compounds prior to chromatographic analysis is a mature technology. Application to low volatility compounds has been far less facile and sensitive. The development of PLOT-cryoadsorption in 2006 resulted in more facile characterization of vapor samples, with applications in explosives detection, food safety, cadaver detection, pyrolysis products and arson fire debris characterization. These laboratory applications were followed by the development of a field portable instrument that has been used for environmental sampling. Further advances of PLOT-cryo technology will require the miniaturization of the components, and the introduction of an in situ solvent reservoir. In this talk, we introduce the first in a series of micro scaled, disposable PLOT-cryo wafers that feature on board Peltier cooling, an on board solvent reservoir, and an injection means capable of delivering an eluted sample to an analytical device.
In-Plane Thermal Conductivity Measurement of Bulk and Thin Film Samples Using Ultrafast Laser-Based Transient Thermoreflectance by Varying Spot Sizes of Laser Beams

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Transient thermoreflectance technique using ultrafast lasers has been well adopted for measuring the thermal conductivity of both bulk and thin film materials and interface thermal conductance. However, it still remains a great challenge to use this technique to measure in-plan thermal conductivity. In this work, we demonstrate an easy and fast way to measure the in-plane thermal conductivity of bulk and thin film samples using ultrafast laser-based transient thermoreflectance method by varying spot sizes of laser beams. A comparison is made between the proposed technique with the previously reported "beam offset" method.
Black phosphorus is a layered van der Waals material, which could have potential applications in electronics and optoelectronics due to its intriguing properties. In this work, we study the phonon transport and thermal conductivity in bulk black phosphorus using the state-of-art first-principles-based Boltzmann transport equation method. Large degree of anisotropicity of its thermal conductivity is observed along three crystal axes. In contrary to the conventional wisdom that the anisotropicity of the thermal conduction of an anisotropic material comes from the group velocity of phonons, we identify the important roles of direction-dependent phonon relaxation times. The anisotropicity of phonon relaxation times comes from the different response of phonon population under the heat flux along different directions.
There have been increasing interests in hybrid inorganic-organic materials, which could combine the strengths of both components, for example, good electronic properties from inorganic part and superb flexibility and easiness in synthesis from organic part. Unlike the electronic and mechanical properties, the thermal properties of hybrid materials are rarely investigated. Understanding thermal properties of the hybrid materials is critical for the deployment of these materials for electronics and optoelectronics since it affects the reliability. In addition, hybrid materials could be explored for potential applications in thermal management and storage. In this project, ZnTe(en)$_{0.5}$, a layered hybrid crystal whose organic chain and inorganic layers are connected by covalent bonds, will be chosen as a first attempt to understand the thermal transport mechanisms in the class II hybrid materials. Such a hybrid crystal with covalent bonding could exhibit quite different thermal transport properties from class I hybrid materials with weak bonding, such as van der Waals or hydrogen bonding. An integrated density-functional theory (DFT) and molecular dynamics (MD) simulation tool will be developed to study the phonon transport properties in ZnTe(en)$_{0.5}$, where the interatomic potentials is developed by fitting a series of properties of ZnTe(en)$_{0.5}$ calculated from DFT calculations and the MD simulations is then conducted to predict its thermal conductivity.
Viscosity Measurements of Hydrate Slurries Formed from Water-In-Oil Model Emulsions

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Viscosity measurements for methane hydrate slurries were performed using a high pressure rheometer with a straight vane impeller as a stirring system. Measurements were conducted using model water-in-oil emulsions to ensure reproducibility of the results (cf.[1]). The model emulsion consists of mineral oil 350T, water, and a surfactant mixture of sorbitane monooleate 80 (Span 80) and sodium di-2-ethylhexylsulfosuccinate (Aerosol OT, AOT). The emulsions that could be prepared with a water content (water cut), of up to 30 vol.%, are highly stable with no phase separation for up to one week, and have water droplets in the range of 2-5 µm. A general equation that describes the viscosity of the emulsion as a function of the temperature, pressure and water cut was developed. This general equation was then used as a baseline to analyze the effect of hydrate formation on the transportability of gas hydrate slurries. Results of this work are presented in terms of the viscosity of the hydrate slurry relative to the viscosity of the emulsion or continuous phase at similar temperature and pressure conditions. In addition, the results obtained in this work are compared with recent flowloop measurements. This allows further analysis and comparison between laboratory-scale rheometer measurements and large scale flowloop tests.

References

Transportation fuels are complex mixtures of numerous compounds, which makes them challenging to study experimentally and computationally. Thus, surrogate fuels having a smaller number of constituents are prepared with similar physical and chemical properties to enable computational simulations. Surrogate fuel modeling for transportation fuels opens a wide window of prospects for designing fuels to obtain higher efficiency and lower emissions. Ideally a surrogate fuel should be tailored to encompass all pertinent physical and chemical aspects of the real fuel to accurately mimic its combustion performance. While formulating surrogate blends, certain target properties of the real fuel are selected based on their relevance towards intended applications. This approach has proven to be decisive while studying new fuels for which combustors are yet to be optimized. The present work introduces thermophysical and thermochemical surrogate mixtures of several gasoline fuels. The surrogates are formulated using a computational model with property simulations and a regression algorithm to find optimal surrogates matching a range of target properties. The target fuels include six FACE (Fuel for Advanced Combustion Engines) gasolines and two certification gasolines. The target properties include hydrogen/carbon (H/C) ratio, density, distillation characteristics, carbon types, heat capacity, enthalpy of formation, enthalpy of combustion, and entropy of formation. The results of simulations and experiments are presented to validate the surrogate fuels
Emissivity Measurements of Semitransparent Coatings and Low Emitting Surfaces

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The ability to determine the emissivity of low emitting surfaces with low uncertainties is necessary for applications where heat losses shall be minimized. For example, a systematically reduction of the heat losses of solar thermal absorber coatings in the mid infrared by variation of the composition of the coatings is only feasible if uncertainties in emissivity measurement of 0.005 are achieved. Another example is the temperature control in forming processes of medical reconstruction parts which is very critical. If done by radiation thermometry it requires precise emittance values of often very low emitting metals or alloys. The direct measurement of the emissivity of low emitting surfaces is possible if multiple reflections between the sample and the surrounding in the measurement setup are taken into account. We present the experimental setup within the Reduced Background Calibration Facility (RBCF) at Physikalisch-Technische Bundesanstalt (PTB) and give a detailed description of our evaluation procedure. We also show that coatings if characterized up to the far infrared often become transparent and that the obtained results can be well explained by taking multiple reflections within the coating and interference effects into account. An observed phase difference between emissivity and reflectivity measurements of semitransparent samples can be explained by a physical model for each measurement approach.
Evaluation of New Experimental Data as Part of the NIST-Journal Cooperation: Modeling Applications

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TRC/NIST has an established cooperation with five major journals in the field of thermodynamics, thermophysics, and thermochemistry: the Journal of Chemical and Engineering Data, Fluid Phase Equilibria, The Journal of Chemical Thermodynamics, International Journal of Thermophysics, and Thermochimica Acta. Prior to publication, newly measured experimental data are evaluated by data experts using ThermoData Engine for completeness of description, physical consistency, and consistency with the existing literature. Experience in dynamic data evaluation at TRC/NIST has shown that interpretation of a data set through the lens of physical models is necessary for proper assessment of experimental data. There are different aspects of data quality assessment facilitated by modeling: mutual consistency within the same data set, consistency with available literature data, physical validity of model parameters, consistency of different properties interrelated by thermodynamic relations, and reasonable variation in a series of similar substances. A wide range of conclusions can be drawn on the basis of modeling, from invalidation of erroneous results to determination of data reliability, from revealing anomalies to supporting unexpected results. Several examples will be shown to illustrate application of property data modeling. With the current level of development in this field, it seems crucial that modeling should supplement any experimental research to support measured data.
We have developed a differential microwave hygrometer (DMWH) for the measurement of the water vapor concentration in gases, in a wide dynamic range from some parts-per-million in volume (ppmv) to 1E5 ppmv. The DMWH measures the polarizability change in a moist gas in relation to the same gas devoid of humidity. The change is proportional to the shift of resonance frequencies in a microwave quasi-spherical resonator filled with the moist gas, in relation to another nearly identical resonator filled by the same dry gas. Differential measurement is used to remove any dependency of frequency shifts from gas pressure and temperature variations. In order to be able to measure low moisture content, pressure and temperature are controlled in both resonators. Temperature uniformity of both resonators is obtained using copper resonators and ensuring a strong thermal link between them. A temperature controlled vacuum enclosure is used to control the resonator’s temperatures at the level of few millikelvin. A quasi-prolate spheroidal geometry is chosen for the inner surface of the resonator, in order to split the degenerate triplet for the TM11 and TE11 microwave modes of a perfect sphere. The frequency lock is based on a very robust and fast modified version of the Drever-Pound-Hall technique. The instrument is compared directly in terms of humidity using a reference chilled mirror hygrometer and shows a great sensitivity to moisture over the whole measured range. Due to its dependency only on frequency standards, the DMWH is a promising instrument for accurate humidity measurements on a large scale of moisture concentrations.
Beyond Lennard-Jones: Global Optimization of Force Fields for Organic Compounds

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Vapor pressure, critical properties, saturated liquid density, and compressed fluid density are used to characterize step potentials for n-alkanes and noble gases. Several potential models were tested to identify the most accurate. These include the Mie potential, the 14-12-8-6 potential, the exp-6, and the two-fluid Yukawa models. Data for the n-alkanes and noble gases include high temperature compressed fluid data that are sensitive to the softness of the potential, which turns out to be an important distinguishing factor. Optimization is facilitated by thermodynamic perturbation theory (TPT) combined with molecular dynamics of continuous potential models (CMD) using the LAMMPS simulator and Monte Carlo simulations (CMC) using GOMC and CASSANDRA. Reference fluid simulations can be performed for a range of potential parameters, with special attention to the repulsive characteristic (e.g. “m” in the m-6 Mie potential). Reference simulations are supplemented with limited simulations of the full potential with “draft” candidates for the optimal potential model, permitting the characterization of complete equations of state that permit variable values of the potential parameters. The methodology follows the publications of Ghobadi and Elliott (J. Chem. Phys., 141:094708, 141:024708, 140:234104). The potential parameters can then be optimized without further simulation. The optimized potentials are tested with full potential simulations. Vapor pressure deviations average near 5% for n-alkanes modeled with transferable united atom models, and 3% for noble gases. Saturated liquid density deviations average near 0.5% below a reduced temperature of 0.9. Compressed fluid densities deviations average near 0.3% for the better potential models. Critical temperatures are matched to within 1K. Critical pressures are matched to within 0.1MPa and critical densities are matched to within 0.01 g/cm³. These results establish a firm foundation for optimal force field development going forward to encompass branches, rings, alcohols, amines, etc.
In recent work, we characterized the repulsive and attractive contributions to the Helmholtz energy of realistic molecular fluids via adaptation of a third-order Weeks-Chandler-Andersen (WCA) perturbation theory [Ghobadi and Elliott, J. Chem. Phys. 139, 234104 (2013)]. In the process, fused soft chains of varying length were simulated interacting with WCA potential at several densities and temperatures, covering the entire phase diagram. Perturbation contributions were computed using the configurations of the purely repulsive reference term. The resulting EOS, referred to as the SAFT-? WCA EOS, provided accurate agreement with the thermophysical properties of pure fluids and mixtures. Consistent with the findings of Avendano et al [J. Phys. Chem. B 115, 11154 (2011) and J. Phys. Chem. B 117, 2717 (2013)], the inclusion of the third-order perturbation term substantially improved the predictions of the EOS in the critical region. Furthermore, it appears that the third-order term can be correlated by scaling the second-order term with a Gaussian function. In this work, we assume that the higher-order perturbation terms follow the same trend and test two methods for resuming the series to infinite order. From a physical perspective, this renormalization function incorporates the impact of the long-range density fluctuations on the thermophysical properties. We demonstrate that one can obtain a remarkable agreement with experimental critical pressure, temperature, and density without sacrificing accuracy outside the critical region. To capture anomalies of derivative properties such as heat capacity at the critical point, we augment the extrapolated TPT EOS with a correction term, originally proposed by Span and Wagner [J. Phys. Chem. Ref. Data 25, 1509 (1996)]. Similar to the Span Wagner application, the extrapolated EOS is very close in the critical region and the augmented term focuses on the non-classical correction. We show how the non-classical correction can be generalized to apply to a range of hydrocarbons. The extrapolation procedure can also be applied to other implementations of perturbation theory. We provide an application to the PC-SAFT EOS to support the generality of the proposed scheme. Comparing to the procedures that are based on Renormalization Group (RG) Theory, application of the G-function is simpler and less computationally expensive. It requires no iteration on the Helmholtz free energy and does not involve numerical integration or differentiation. The extension to mixtures and long-chain molecules is also carried out in a straightforward way without sacrificing the accuracy or introducing additional adjustable parameters. With this approach, perturbation theory can provide accuracy that is competitive with multiparameter equations in the critical region.
Towards a Reliable Method for Automated Thermography Welds Inspection: Algorithms for False Positives Discarding

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Non Destructive Testing (NDT) by Infrared Thermography is one of the most promising techniques for replacing traditional operator-dependent NDTs such as Liquid Penetrant, Magnetic Particles or Visual Inspection. This fast and noncontact technique is one of the most suitable ones to be automated for working under difficult or extreme conditions, where the presence of an operator might be unsafe. Nevertheless, evaluation strategies developed up to now reveal that clear discarding between real defects and false positives remains still a challenge. In this work the problem of false positives identification when inspecting welds is addressed. Welds inspection becomes crucial to assure safety in critical applications since surface breaking cracks could grow rapidly under high load or temperature conditions. A thermographic system with a continuous laser line excitation inspects automatically the weld joints in order to detect surface breaking defects. When usual spatial processing techniques are applied, defects may be identified. But in addition to them, indications referring to emissivity variations, i.e., surface heterogeneities and/or contamination (among others) are also found. Here, various spatial and temporal algorithms have been combined and applied to accurately discard false positives from real defects when inspecting welds. Therefore, the feasibility of automated Infrared Thermography inspection for replacing traditional operator-dependent techniques is proved.
Radiative property measurements at high temperature have to deal with a number of challenges, including possible sample contamination from the container or surrounding space, as well as contamination of collecting optic or windows by evaporated sample material. Fast measurement techniques allow one to deal with both of the above issues at the price of a very limited integration time and an inability to implement measurement methods requiring sequential measurements. We are proposing a new DYME (DYnamic Meltpool Emissometry) technique, which combines a very short exposure of any part of the sample to high temperature together with an ability to provide several seconds of measurement time. This enables us to realize measurement of complex sequences. In our approach, reflectance and emittance measurements are performed dynamically with in-line (shared with a heating high-power laser) registration of the optical path, which includes a 2D optical scanner. We are able to treat a fast moving melt pool (or a hot spot) as a static measurement target, while providing better tolerance to the residual oxygen levels, reduced sample contamination, and fewer issues with sample evaporation (due to the small area of the heated zone). This method will become a core element of the new TEMPS (Temperature and Emittance of Melts, Powders and Solids) facility under construction at NIST. TEMPS is aimed at significant improvement of our understanding of emissive properties of metals, ceramics and polymers in different aggregate states in the visible and thermal infrared at temperatures up to 3500 K (and potentially higher) in a vacuum or a low-oxygen purge gas environment. TEMPS will be co-located with another facility, related to Additive Manufacturing research, which is beyond the scope of this presentation.
Quality control of the performance of mechanical components subjected to hardness processing is a topic of fundamental importance, both in the field of automotive and aerospace systems both for civil and military applications. The lack of cementation, the burns in the steels, and the decarburisations of the power gears, and the statoric and rotoric equipments may cause catastrophic failures with serious repercussions. The industry and the companies responsible for the hardening processes as well as for the quality control of the mechanical components are continuously seeking for improvements in the standard destructive tests performed by Vicker or Brinell durometer where one mechanical component is chosen for random testing. In the last years we developed a new PTR compact system, integrable with mechanized and robotic arms for industrial needs, which use a simple Ge lens for collecting the IR radiation from the sample to the detector. The inverse problem to reconstruct the diffusivity profile $D(z)$ from the PTR signal in the frequency domain $S(f)$ has been solved by using different inversion techniques. We present here some results on AISI9310 hardened steel gears where we compare the hardness profile reconstructions measured by Vicker test with the photothermal reconstructions obtained with different inverse procedures.
Thermochromic materials, changing their spectral properties as a function of the temperature, are extensively studied in the search for active control of thermal emission. These are for example niobium dioxide (NbO2), vanadium sesquioxide (V2O3) and vanadium dioxide (VO2). We present here a detailed infrared study of the semiconductor-to-metal transition (SMT) in a vanadium dioxide (VO2) film deposited on silicon wafer. The VO2 phase transition is studied in the mid-infrared (MIR) region by analyzing the transmittance, reflectance and emittance measurements. The temperature behaviour of the emissivity during the SMT put into evidence the phenomenon of the anomalous absorption in VO2 which has been explained by applying the Maxwell Garnett effective medium approximation theory, together with a strong hysteresis phenomenon, both useful to design tunable thermal devices to be applied for the thermal control of spacecraft. We have also applied the photothermal radiometry in order to study the changes in the modulated emissivity induced by laser. As example we present and compare the experimental results obtained on a single layer of vanadium dioxide, and of a multilayer VO2/Cu designed so to maximize the tenability of emissivity. The experimental results show how the use of these techniques represent a good tool for a quantitative measurement of the optothermal properties of vanadium dioxide based structures. This work has been performed in the framework of a collaboration between Sapienza University of Rome and the Defence R&D Canada Valcartier research center. Part of the work has been granted by Italian Ministry of Defence.

References

Nondestructive Analysis of Phytochemicals Present in Typical Foods of the Mediterranean Diet by Photoacoustic Techniques

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Many epidemiological studies suggest that a diet rich in fruits and vegetables, like the Mediterranean diet, offers protection against some common diseases of the Western world, such as cardiovascular events, obesity, diabetes, cancer and other age-related degenerative diseases. Fruits an vegetable have long been regarded as having considerable beneficial effects on health, due in part, to the presence of bioactive compounds or phytochemicals. These compounds include tens of thousands of molecules belonging to various chemical classes and botanical families also very distant from each other such as carotenoids, tocopherols, glucosinolates and polyphenols. They are produced as secondary metabolites by plants and play a key role in complex biotic and abiotic interaction. In fact, the bioactive compounds are essential for plants survival, because are produced, as signal molecules, in response to various stimuli including stress (UV, temperature, hydric stress). Their amount and composition in plant foods is strongly dependent on a number of factors as genotype, ripening, environmental conditions, climate, cultivation practices, harvesting modalities and storage methods. Moreover, many of them are responsible for the organoleptic characteristics of foods such as colour, aroma and taste. In the human organism, the phytochemicals, through different mechanisms, defend our cells and tissues from free radicals attack, helping to neutralize or reduce the oxidative processes. In particular, due to their chemical structure, the phenolic compounds may exert strong antioxidant activity, in addition these molecules are involved in several other cellular processes, for example, are able to interact and modulate multi-enzymatic systems, to inhibit platelet aggregation, to counteract the carcinogenesis, to reduce the formation of inflammatory molecules. The daily and continuous introduction of these substances is of particular importance for human health. All these properties confer to phytochemical an important role as biomarkers of nutritional, healthy and commercial quality. Nowadays, both the food industry and the agricultural sector need of rapid screening tools that make it possible the quality control along the whole chain of production (from farm to finished product). In this respect is desirable a non-destructive analytical approach, which allows to correlate the information obtained from direct analysis of bioactive compounds content in plant foods with the stadium of ripeness, freshness, shelf life of products. In the recent years, the PA and PT techniques have been applied to the quantitative analysis of phytochemicals present in fruits and vegetables. In particular, these techniques have allowed the direct quantitative analysis of carotenoids (a- and ß-carotene, lycopene) and flavonoids (mainly anthocyanins) in fresh produce products such as tomatoes, carrots, brassicaceae, oranges, cherries, apricots, grapes, wine, etc, with little or no manipulation of the sample. In particular we obtained preliminary data (figure 4) from PA signals measurements in peel of apple fruits belonging to two different varieties: Golden Delicious and Royal Gala. The results revealed that PA signals were in agreement with the presence of chlorophylls (a and b), carotenoids and anthocyanins in different side of apple according to the different colour of the portion of apple peel analysed.
Nondestructive Evaluation of the Thermoelastic Properties of Contact Lenses by Photothermal Deflection Technique

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Mechanical characteristics of soft contact lens material are critical in design, quality control processes, properties and comfort. Most soft contact lenses are made of hydrogels. Mechanical properties such as elastic modulus, stiffness, flexural rigidity and viscoelasticity thus have major impact on the ability to maintain the physical geometry and dimension, on the capability to return to the original shape at removal of external load, on the adhesion to the cornea, and swelling behavior and proliferation of cells. Moreover soft contact lenses are commonly used to correct refractive errors of the eye and protect the ocular surface from ocular damage and after corneal surgery. Monitoring the intraocular pressure is an essential part of daily clinic activity, and tonometry through the soft contact lenses is convenient especially when treating subjects with ocular surface diseases. The effects of conventional soft contact lenses of low power on the intraocular pressure have been reported to be negligible. Nevertheless, other studies have found that the intraocular pressure measured on non-contact tonometry through soft contact lenses is altered and that the changes depend on the lens power, curvature, thickness and rigidity. All these critical points strongly motivate the need of methods for an accurate local mechanical and thermal characterization of contact lenses. The current mechanical characterization technique is to cut a rectangular strip before measuring the stress-strain relationship using a standard universal testing machine. The elastic modulus and Poisson ratio can thus be deduced from the data obtained. Obviously such a destructive technique cannot be applied when the contact lens is on the cornea. We introduce here a photothermal method to perform the non-destructive evaluation of the thermoelastic properties of the contact lenses. The method is based on the photothermal deflection technique where a pump laser beam is focus onto the sample so as to induce a surface thermoelastic displacement. A probe beam is sent to the deformed area of the sample which causes a change in the direction of the reflected probe beam, easily detected by a position sensor. By scanning the whole area it is possible to reconstruct and map the shape of the induced displacement. Preliminary measurements performed on various contact lenses show how is possible to detect displacements of the order of a few Angstroms and evaluate the thermal expansion of the lenses. In this work we will also discuss and compare the results obtained on several soft and hard contact lenses.
By design, most engineering processes are only weakly sensitive to their inputs, including thermophysical property data. On rare occasions, highly accurate thermophysical property data are needed, for example, to tightly control a process, to optimize efficiency, to meter a high value product, or to determine the thermodynamic temperature. Where can we get such highly accurate data? In the 21st century, the most accurate thermophysical property data for any gas is generated by quantum-mechanical calculations of the properties of helium, even at densities well above the dilute gas regime. When we use the calculated properties of helium as standards, we can understand and/or calibrate laboratory apparatus in remarkable detail. Then, carefully selected ratio measurements determine accurate working standards for temperature, equation-of-state, dielectric constant, thermal conductivity, viscosity, speed of sound, and the flow of gases. A chain of ratio measurement leads from helium to argon and ultimately to industrially important gases such as moist air and the reactive gases used to process semiconductors. Ratio measurements can also refine the parameters in model interatomic and intermolecular potentials. Then, model potentials can be used to accurately predict thermophysical properties of gases at high temperatures and pressures, where accurate measurements are difficult.
A numerical value as a result of a measurement of a thermophysical property is meaningless without an assessment of the quality of that value. Early attempts by evaluators to assess data quality were hampered by the different meanings given to the various terms used to describe accuracy in measurements. Some of the earlier attempts to clarify the terms used to describe data quality and to assist experimentalist to either check the quality of their measurements or calibrate their equipment through the use of reference materials will be discussed. The publication by the International Organization for Standardization (ISO) of the Guide to the Expression of Uncertainty in Measurement in 1993 allowed authors and evaluators to start to standardize the terms used in assessing data quality in reported measurements. The major problem facing an evaluator of published thermophysical property data is determining what the authors mean when providing values of uncertainties. The major journals publishing thermophysical property data now require the authors to provide uncertainties at a specified level of confidence for all the measurement variables. Usually sufficient information about Type A uncertainties (uncertainties due to statistical variations in multiple measurements) is given by the authors. However the information given regarding Type B uncertainties (those based on scientific judgment using all the relevant information available including previous measurements, purity of materials, experience with the use of the instruments, manufacturer’s specifications, calibrations, and uncertainties assigned as a result of measurements made with reference materials) is usually inadequate, often resulting in the evaluator rejecting the authors’ assessment. Various examples of the pitfalls faced by an evaluator evaluating Type B uncertainties in thermophysical property measurements will be given. Once the quality of the data has been established, different database systems store the evaluation in different ways depending on the final use of the evaluated data. Various approaches will be discussed. These variations result in difficulties in developing robust data exchange protocols.
Correlation of Thermal Conductivity with Vacancies and Dislocations in High Purity Nb at 2-4 K.

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Superconducting Nb cavities, as used in particle accelerators, operate efficiently at temperatures of 2-4 K. A contributing factor to the high efficiency is maintaining large values of thermal conductivity $k$, which enhances heat dissipation into the He bath arising from local defects on the RF surface. For $T < 3$ K, with conductivity $k_3$, the dominant mode of heat conduction is by phonons, with a local maximum $k_{pp}$ occurring at about 1.8 K. Vacancies and dislocations can disperse phonons that have trajectories toward the outer wall, and thus reduce $k$. There is keen interest in understanding the relationship between $k$ and the manufacturing processes employed to making a cavity. The relationship between the variation of $k$ and pre-existing dislocations, dislocation substructures, deformation, and annealing phenomena is examined. Orientation gradient maps were generated for Nb specimens in their as-received condition and after 2 h heating under vacuum. Local average misorientation (LAM) maps indicate the spatial arrangement of geometrically necessary dislocations. One specimen in its as-received condition had the lowest amplitude and widest LAM distribution, indicating a higher fraction of dislocations were present within this one specimen. The LAM following heat treatment for 2 h at a temperatures of 600, 800, 1000, or 1200 °C indicated that a significant reduction of dislocation density occurred at 1000 and 1200 °C. The LAM distribution for these specimens did not correlate directly with the recovery of the phonon peak in $k$. The discrepancy may stem from inadequate sample size on the surface. The bulk measurement of $k$ examines a much larger volume. Thus, high-energy x-ray diffraction was performed to test this hypothesis. Diffracted peak broadening corresponding to the {222} slip directions was used to estimate qualitatively dislocation and imperfection content of the specimens by comparing the full width at half maximum of the diffraction peaks (FWHM) for the four specimens. The specimen heat-treated at 1000 °C had the smallest FWHM, implying the fewest crystal imperfections in that specimen. The higher defect density at 1200 °C may reflect a higher vacancy concentration, as there were few sites available to absorb vacancies. Taken together, the normalized phonon peak ($k_{pp}/k_3$) is sensitive to both dislocation and vacancy densities.
Theoretical approach based on the concept of “complete scaling” has been extended to multicomponent mixtures. The approach does not depend on the number of mixture components provided that the average mixture composition is fixed. It has been shown that all thermodynamic values of multicomponent mixture can be parameterized in a universal way by means of two independent scaling fields of 3D-Ising model. As a result, the equation of state (EOS) for near-critical mixture with given composition has been formulated. The EOS allows calculating various thermodynamic properties, in particular, the derivative \( \left( \frac{\partial P}{\partial T} \right)_{\rho, x} \), the isochoric heat capacity \( C_{\rho, x} \) and the equation for dew-bubble curves in the vicinity of liquid-vapor critical points in mixtures. It has been shown that \( \left( \frac{\partial P}{\partial T} \right)_{\rho, x} \), the heat capacity \( C_{\rho, x} \) and the second derivatives \( d^2 \frac{\partial T}{\partial \rho^2} \) and \( d^2 \frac{\partial P}{\partial \rho^2} \) (taken along the dew-bubble curves) reveal cusp-like anomalies at the critical point. This specific feature enables us to propose a simple method for the estimation of the critical parameters of multicomponent mixtures. To verify the validity of the obtained EOS, it was applied for the description of experimentally studied thermodynamic properties of several binary, ternary and multicomponent mixtures. The measurements of the pressure, the derivative \( \left( \frac{\partial P}{\partial T} \right)_{\rho, x} \) and the heat capacity \( C_{\rho, x} \) were carried out along the isochores in a wide range of temperatures including the near-critical region. It has been demonstrated that the proposed EOS describes adequately the experimental data in one- and two-phase region of the mixtures.
Amorphous thin-films are integral components in all integrated circuits. As devices are miniaturized, they routinely encounter heat dissipation problems. For amorphous thin-films, a robust model – beyond the Cahill-Pohl or Einstein models – for predicting their thermal conductivity is needed. More generally, little is understood about the fundamental microscale physics that underpins thermal conductivity in amorphous materials and much can be learned about the vibrations in amorphous materials. With this goal in mind, we developed an empirical model based on Allen-Feldman’s classification of vibrational modes – vibrons, which are divided into propagon, diffusons, and locons. In the presented work we investigate the low temperature (~10-30 K) thermal conductivity of amorphous polymer films, to better understand the nature of the propagating modes, using the well-established 3-omega technique. This technique was selected because of its accuracy at low temperature. Using these results, we establish cut-off frequencies and temperatures that correspond to modal transitions. We then extend this empirical model to understand vibrational modes that are more diffusive in nature, and vibrational modes that are more localized in nature. Using this model we are able to extract characteristic thermal length-scales, which then provide us with the engineering tools to control the thermal conductivity in these materials.
Effects of Resins on Aggregation and Stability of Asphaltenes

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Effects of the addition of resins on aggregation and stability of petroleum asphaltenes in hydrocarbon solutions were studied by dynamic light scattering. Average aggregate size as a function of the concentration of the precipitant (heptane) and upon the addition of resins was monitored in real time. It is shown that resins serve as inhibitors for asphaltene aggregation, shifting the onset of aggregation. However, the dependence of the onset on the concentration of resins has a tendency to saturate. The characteristic time of aggregation decreases exponentially upon increase of the precipitant concentration, while it grows linearly upon increase of the concentration of resins. A definition of the onset of asphaltene aggregation based on the time dependence of the aggregate-size growth is suggested. It is also shown for all the samples studied (with and without resins) that the aggregation is controlled by diffusion-limited kinetics. The size of the aggregates as a function of time follows a diffusion-limited-kinetics power law with an exponent $\alpha = 0.36\pm0.04$, which is related to the fractal dimension $d_f$ of asphaltene clusters as $\alpha=1/(1+d_f)$. 
Thermal Conductivity and Shear Viscosity of n-Decane and n-Hexadecane with Nanoparticle Suspensions using Molecular Simulations

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Atomistic molecular dynamics simulations were carried out at equilibrium to calculate the constant pressure shear viscosity and thermal conductivity of n-decane and n-hexadecane within the range of ambient to extreme temperature and pressure conditions (i.e. up to 500 °F and 35,000 psi). A quantitative comparison of the results was performed against experimental values and values predicted from a high temperature - high pressure perturbed chain - statistically associated fluid theory (HPHT PC-SAFT) model. In addition, the effect of the presence of Lennard-Jones nanoparticle suspensions was also analyzed for volume fractions of up to 1%. Analysis of the intra- and inter-molecular structure of the fluid as well as its dynamical characteristics were also performed.
There is a growing recognition that heavy hydrocarbon resources such as Maya crude oil from Mexico, and Athabasca bitumen from Canada, and heavy hydrocarbon resource fractions, such as Safaniya vacuum residue from Saudi Arabia are multiphase fluids [1-3] and exhibit non-Newtonian rheological behaviors [4] particularly at low temperatures. In this work, the phase behaviour of such fluids is briefly reviewed and the deviation between an integrated heavy oil characterization and Newtonian viscosity prediction approach [5,6] and complex viscosity data sets comprising whole crudes and whole crudes partitioned using nanofiltration, without solvent addition, into pentane asphaltene enriched retentates and maltene enriched permeates, as well as chemically separated maltene and asphaltene fractions is examined. The range of asphaltene contents in the nanofiltered samples is ~ 2 to ~ 70 wt %. The data sets include steady shear rheology measurements ranging from 0.1 to 50 s⁻¹, and oscillatory shear measurements where shear amplitude is varied as well as shear frequency. In this exploratory work, systematic deviations between measured and predicted viscosities are probed so that the impacts of oil characterization and non-Newtonian behaviours on the quality of viscosity prediction can be parsed. Impacts of characterization on prediction quality are identified under conditions of temperature and composition where Newtonian behaviour obtains. Non-Newtonian contributions to viscosity are identified in the balance of data sets. Deviations exceeding an order of magnitude are observed under industrially relevant conditions. The contributions of characterization, maltene phase behavior, and asphaltene content to these systematic deviations are presented and discussed.

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From Low Temperatures to High: Systematic Manipulation of Ion Structures to Achieve Low Melting Points and High Decomposition Temperatures

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Our group is keenly interested in probing and learning to systematically manipulate the relationship between the structure of IL ions and their thermal properties - both their melting points and their decomposition temperatures. We have discovered that, by-in-large, the structural characteristics that give rise to low melting points are often inconsistent with achieving truly high degrees of high-T stability (i.e., stability to T > 250 for months). This has resulted in our efforts being bifurcated into parallel projects in which the objective of one is the achievement of low $T_m$ values with retention of moderate thermal stabilities, while the objective of the other is the achievement of very high thermal stabilities in conjunction with workably low values of $T_m$. In the former case, we have made considerable progress in achieving low $T_m$ values in relatively large-ion ILs by building on the biological principle of the homeoviscous adaptation of cell membranes. Specifically, we found the incorporation of alkene-groups in IL cation side chains predictably results in lower values of $T_m$ relative to counterparts with saturated side chains. Most recently, we have found that this effect is also imparted to ILs by the incorporation of thioether groups into ion side chains. In terms of ILs stable to high temperatures, we have found that there appears to be a quite limited scope of structural and compositional elements consistent with the creation of molecular cations with high long-term thermal stability. In this talk we will discuss in detail what these elements are, as well as discuss why this is the case. Overall, we will endeavor to provide a conceptual toolkit which others may find useful in making informed choices of ion design to create ILs with particular thermal characteristics.
A substantial part of the research effort in the field of ionic liquids (ILs) is dedicated to the study of their organization at the molecular level. The nano-structuration of these fluids gives rise to many of their peculiar properties, both in the pure state and in the interaction with other substances. Its understanding is thus fundamental to the rationalization of IL behavior. A wide range of techniques has been applied with that purpose, from X-ray and neutron diffraction to molecular simulations. Spectroscopic techniques, using appropriate probes, have also been applied to the study of the nano-structuration of ILs, with the advantage of their accessibility and non-destructive nature. The NMR active $^{129}$Xe nucleus is very sensitive to the local molecular environment around it, due to the large electron cloud and high polarizability of the xenon atom. Depending only on the solvent, $^{129}$Xe presents a range of chemical shifts over 250 ppm. Moreover, its small size as opposed to the usual spectroscopic probes (e.g. fluorescence, solvatochromic, etc), and the non-specific nature of its intermolecular interactions (only van der Waals forces) assures little perturbation of the liquid structure. In this work, $^{129}$Xe chemical shifts have been obtained, as a function of temperature, for solutions of Xe in a wide range of ionic liquids. Evidence is shown for the change of liquid structure with the increase of the alkyl chain length along a given IL family, for the mobility of Xenon around both polar and apolar domains, and for its preferential location in apolar regions. Molecular
dynamics simulations help to elucidate the NMR results [1]. Particular attention has been dedicated to ILs which display thermotropic liquid crystalline behaviour. It is shown that 129Xe spectroscopy is not only able to identify the isotropic liquid to liquid crystal transition, but is also able to provide insight on the differences between the molecular environments in both phases.

References

An IoNanofluid is defined as a mixture of an ionic liquid with a nanomaterial. The thermal conductivity of several ionic liquids and IoNanofluids has been measured in our laboratory in the latest years between room 293 K and 343 K at 0.1 MPa [1-6]. These studies have shown that the thermal conductivity of the pure ionic liquids and IoNanofluids with MWCNT’s is sensitive to the molecular constitution. The compounds studied can be separated into head group, an aliphatic side chain and an anion. Preliminary conclusions show that: - Changing the side chain length, the enhancement in the thermal conductivity increases, possibly due to a better interaction between this chain and the carbon nanotube surface (non-polar entities) that facilitates heat transfer - The change of the head group does not seem to affect the enhancement very much - For liquids that have the same cation, [C2mim or C4mim], and different anions, [N(CN)2], [C2H5OSO3] and [(CF3SO2)2N], the anion structure affects the enhancement very much - The enhancement in the thermal conductivity is strongly dependent on the weight/volume fraction of the carbon nanotubes present in the IoNanofluid and weakly dependent on temperature - Current nanofluid enhancement theories are not able to predict the values found New data on [P6 6 14][DCA], [P6 6 14][Br] and [C2mim][CN] and their nanosystems with MWCNT’s will be reported. The overall set of results will be used to generalize the preliminary conclusions above. A discussion on the theoretical models for ionic liquids and for the enhancements in the IoNanofluids will also be presented.

References

Spontaneous Multilayering in Langmuir Films of Ionic Liquids at the Air-Water Interface

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Many of the potential applications of ionic liquids (IL) involve processes that take place at interfaces, either at the liquid-vapour interface of a pure IL or solution, or at the surface of other liquids and solids. The study of the interfacial properties of ILs, pure or in solution, is therefore of utmost importance for the development of their technological applications, since their properties can be significantly different from those of the bulk liquids. Despite its obvious importance, the knowledge of the structural properties of ILs at the air/water interface is still quite poor. A better understanding of the behaviour of ILs at this interface can be obtained studying the formation of thin films through the Langmuir and Langmuir-Blodgett techniques. To date, this is a largely unexplored field. To the best of our knowledge, the only existing studies are those of Bai et al1 and Mukherjee et al.2. However, the first study focused essentially on the practical objective of obtaining gold nanoparticles, while the latter addresses the general amphiphilic behavior of the studied ILs. As a result, the structure and stability of the corresponding Langmuir films remains practically unstudied. In this work we have studied the behaviour of a number of ILs of the methyl-imidazolium family at the air-water interface using the Langmuir and Langmuir-Blodgett techniques. Additionally, molecular dynamics simulations have been performed to obtain molecular level insight on the structure of the films. In the case of [octadecylmim][NTf2] and [octadecylmim][Cl] we have obtained for the first time evidence of the spontaneous formation of multilayers of these ionic liquid at the air-water interface. The overall behavior of the films is quite complex.

References
Ionic liquids have proved to be excellent heat transfer fluids and alternatives to common HTFs used in industry for heat exchangers and other heat transfer equipment [1,2]. One of the main arguments against its utilization in large scale units is the cost/kg of the ionic liquids. This argument is based on the selling price of ionic liquids produced at a laboratory level (300-2000 €/kg), where the price is inflated by the labour cost involved in the synthesis of small quantities. Although the cost of tonnage production is not usually disclosed, it is below 20 €/kg (a factor of 15-100 times lower), a value competitive for some industrial applications with biphenyl and diphenyl oxide, alkylated aromatics and dimethyl polysiloxane oils, which degrade above 200ºC and possess some environmental problems.

1-ethyl-3-methylimidazolium methanesulfonate [C2mim][CH3SO3] (CAS Number 145022-45-3), is actually produced by BASF, under the trade name of Basionics® ST 35, with an assay = 95% with = 0.5% water and chloride (Cl-) = 2%. An extensive search about the thermophysical properties of this IL using the ILThermo Database [3] shows that the data available is very scarce for density, viscosity and heat capacity, and non-existent for thermal conductivity. The study of the heat transfer coefficients of this fluids to be used in common heat exchangers (shell and tube, parallel plates, concentric cylinders) requires not only the thermophysical properties involved in the heat transfer process, but also the simulation of the real equipments in a pilot scale. A complete study of the thermophysical properties of [C2mim][CH3SO3] started in our laboratory, with the support of BASF SE. Density, speed of sound, heat capacity, viscosity and thermal conductivity of the industrial product, and after purification, are being obtained for the temperature range 293-353 K. In addition the heat transfer coefficients for the pairs water/IL and water/EG are studied for a parallel plates pilot heat exchanger, comparing the relative global efficiency. Details of the instruments and heat transfer pilot will be given.

Acknowledgements

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References

The NIST Thermodynamics Research Center (NIST/TRC) is one of the oldest data research centers in the United States. For over 70 years of its history, TRC has produced a number of the periodical compilations and electronic databases on thermophysical and thermochemical properties of pure compounds and mixtures that have become a major data source for scientific research and industrial process design. NIST ThermoData Engine (TDE) is curation software that combines algorithmically encoded critical analysis, a comprehensive set of thermophysical and thermochemical property values from the open literature and a range of prediction methodologies to generate a database of recommended values on demand. Two versions of TDE will be demonstrated: Standard Reference Database (SRD) 103a encompassing properties of the pure compounds only and SRD 103b generating critically evaluated data for pure compounds, binary mixtures, ternary mixtures, and chemical reactions. ILThermo (NIST SRD 147, http://ilthermo.boulder.nist.gov/index.html) is a free web application that provides access to experimental thermodynamic and transport properties of neat ionic liquids, as well as binary and ternary mixtures containing ionic liquids, including citation and uncertainty recommendations. NIST Gas Hydrate Database (NIST SRD 156, http://gashydrates.nist.gov/) is a free web application that provides access to experimental thermodynamic and transport properties of gas hydrates and similar clathrates, including citation and uncertainty recommendations. ThermoPlan (NIST SRD 167, http://trc.nist.gov/thermoplan/) is a web application that provides free and open access to the experimental planning utilities powered by TDE. It provides assessment for the merit of a proposed measurement for pure compound or a mixture via assessment of the existing body of knowledge. ThermoLit (NIST SRD 171, http://trc.nist.gov/thermolit/) is a web application that provides free and open access to the literature search capabilities powered by TDE. It reports relevant literature citations and ranges of measurements for pure compound or mixture properties via assessment of the existing body of knowledge. Web Thermo Tables (WTT, Lite Edition - NIST SRD 202, http://wtt-lite.nist.gov/ and Professional Edition - SRD 203, http://wtt-pro.nist.gov/) is a successor of TRC Tables and a web interface for TDE for pure compounds, available to the customers on a subscription basis.
The scientific goal is to achieve the modelling of the thermodynamic (vapor pressure, saturated liquid densities, single-phase liquid densities, compressibility factor, HPHT phase equilibria, interfacial tension, isobaric compressibility, volume expansivity, enthalpy, entropy, internal energy, Gibbs free energy, isobaric and isochoric heat capacities, Joule-Thomson coefficient, speed of sound) and transport (dynamic viscosity, kinematic viscosity, thermal conductivity, thermal diffusivity, molecular diffusivity, dielectric constant, Prandtl number and Eucken number) properties within a single functional framework of applying the same set of parameters used in thermodynamic equation of state in the transport equation of state model. Such a goal has been achieved by the reformed Van der Waals 1873 cubic equation of state, which hereafter has been named the Lawal-Lake-Silberberg (LLS) cubic equation of state. The LLS equation is designed with four physically meaningful parameters that reflect molecular attraction, size, structure and shape for the individual pure substances and it is applicable for predicting thermodynamic and transport properties over the entire PVT states, including fluid vapor-liquid critical point. The thermodynamic equation of state is unified with the caloric and transport equations of state through the judiciously designed Van der Waals Gas-Constant (Rvdw) for ideal-gas behavior. While the LLS equation is built with two continuously differentiable attractive and repulsive temperature functions a(T) and b(T), we are still lacking the generality for the three binary interaction parameters that relate the pure component parameters and composition to the mixture combining rules that are specified for the attractive parameter a(T) and two other parameters that relate the critical compressibility factor predicted by the LLS equation to the composition of mixture thereby guaranteeing stable convergence of gas-liquid properties at far away from, neat to and at the critical point of mixture of fixed overall composition. The versatility of the LLS cubic equation is illustrated with the prediction of accurate volumetric and coexistence gas-liquid densities of asymmetric pure components and the prediction of accurate phase equilibria, saturated liquid densities and critical properties of binary systems.
The Van der Waals Ten Commandments Resulted in Four Empirically-Based Molecular Parameters for the VDW 1873 Equation of State

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As yet, fluids have refused to be boxed into the two-parameter cubic equation of state that Van der Waals (VDW) prepared for them. But, the VDW 1873 theory specified four properties for determining the P, v, T relation of a substance, including the fluid gas-liquid critical point, which is in accord with the four critical constraint criteria used to specify those properties for the VDW theory of cubic equations of state and that also is in agreement with the four parameters stipulated by the theory of cubic polynomial equations of state. Since the VDW theory has acknowledged molecular size and molecular attraction into the 1873 equation, the possibility of including two inspired parameters into the VDW 1873 theory can be inferred from the 1910 Nobel Prize Lecture in which VDW categorically rejected non-molecular based and non-physically meaningful empirical parameters into the 1873 theory, which we have justified by the judiciously constructed VDW Ten commandments for the designers of cubic equations-of-state. By relating the empirical parameters (a, ß) of the Lawal-Lake-Silberberg (LLS) equation to the microscopic force-parameters derived from the statistical mechanics energy potential functions and performing perturbation and other sensitivity analysis; the sensitivity of the derivatives of the structural parameters (Pc, Zc, Tc) and the sensitivity of the derivatives of second, third and fourth virial coefficients with respect to a show non-linear trend with a-parameter and thus, a replicates structure of pure substances in the configuration of the LLS equation. Similar analysis of the derivatives of the critical volume (Vc) and Boyle temperature (TB) with respect to ß show non-linear trend with ß-parameter and thus ß reflects shapes of pure substances in the configuration of the LLS equation. The empirically-based molecular parameters (a, ß) bring the VDW 1873 equation in conformity to the stipulated shapes of the potential energy and length scale of the statistical mechanical potential functions and reconcile the VDW theory with liquid-phase properties and gas-liquid critical point.
Atmospheric plasma spraying is a process in which particles are deposited on a substrate in a molten or semimolten state. Few studies were carried on optical properties about plasma sprayed coatings. Nevertheless, the specific microstructure combined with a wise choice on materials could bring alternative solutions in fields such as solar energy or aeronautic. The aim of this work is to study optical properties of plasma sprayed coatings, for wavelengths from visible to near infrared. To this end, alumina/aluminum cermet coatings were experimentally and numerically realized with different metallic rates ranging from 0 to 100\%wt. Influent parameters (microstructure, roughness, crystallography, composition...) were emphasized. Composition and microstructure of the samples were carefully characterized to explain their optical response, highly dependent on volumetric and/or surface light scattering. Besides their contribution to the knowledge of microstructure, 2D SEM and 3D microtomography images were used to get statistical data in order to generate simplified numerical samples. A Monte Carlo ray-tracing model, based on geometrical optical laws, allowed to simulate material optical behavior and to reproduce experimental trends of optical spectra.
Single-walled carbon nanotubes (SWCNTs) are a versatile electronic material being explored as cost-effective, high-performance active materials in a variety of renewable energy applications such as transparent conducting or light-harvesting layers in photovoltaics and inclusions in thermoelectric composites. We present a series of experiments focused on understanding the thermoelectric performance of enriched semiconducting SWCNT networks dispersed in a semiconducting polymer matrix. Rational choice of the semiconducting polymer allows us to sensitively tune the s-SWCNT diameter and band gap distributions within the composites. We use a stable charge-transfer dopant to control the density of carriers in the s-SWCNT network, as determined by the bleach of the absorption corresponding to the S11 excitonic transition. The performance of these transparent conducting s-SWCNT composite networks is comparable to neat p-type and n-type s-SWCNT networks doped by either nitric acid or hydrazine treatments. By varying the carrier density we are able to probe the relationship between the electrical conductivity and Seebeck coefficient (thermopower) in the s-SWCNT networks as a function of the carrier density and position of the Fermi energy. Although the electrical conductivity of the s-SWCNT networks is poor at very low carrier densities we have measured a colossal thermopower as high as $\sim2,500 \, \mu V/K$, which is more than an order of magnitude larger than has been previously reported for SWCNT-based material systems and is consistent with theoretical calculations that consider the density of electronic states in individual s-SWCNTs. As we tune the carrier density, we are able to maintain a thermopower above 200 $\mu V/K$ over almost the entire range of hole densities, corresponding to conductivities up to 1885 S/m, resulting in a thermoelectric power factor of $\sim100 \, \mu W/m\cdot K^2$. These studies suggest that the low dimensionality of the SWCNTs has a stronger impact on the electrical conductivity than the thermopower, implying that they are less strongly coupled in these systems than is observed for compound inorganic semiconductors. We also present a sensitive technique, based on a microfabricated silicon nitride thermal isolation platform, to probe the thermal conductivity in the s-SWCNT networks, allowing us to estimate the thermoelectric figure of merit ($zT$) for these materials to be $\sim 0.01$. These observations demonstrate the ability to exert exquisite control of the thermoelectric performance by tuning the carrier density and/or Fermi energy, and touts SWCNTs as an avenue for realizing thermally stable room temperature thermoelectric devices fashioned from inexpensive and abundant organic constituents.
Wettability of 12Cr18Ni10Ti Reactor Steel by the Eutectic Alloy of PbBiLi

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The Pb44.5Bi55.5 eutectic alloy and its components are used as coolants in nuclear power plants, heat pipes, etc. [1, 2]. In the presented study the temperature dependence (TD) of wettability of 12Cr18Ni10Ti reactor steel by the eutectic alloy of PbBi and its ternary alloys with up to 20at.% of Li was measured, for the first time, in vacuum and in purified argon atmosphere. The eutectic alloy was prepared using Pb and Bi with no less than 99.9999% of the basis element. The measurement chamber included a high-resolution CMOS video camera that allowed imaging the alloy drops at no less than 5 frames per second. The drop profiles were automatically captured, processed, and the contact angles were determined using the sessile-drop method, with an error of 1.5% [3]. The wettability of 12Cr18Ni10Ti reactor steel by the eutectic alloy of PbBi was studied in the wide range of temperatures from the melting point to 1520 K. The temperature was controlled with the accuracy of ±0.1K using a chromel-copel thermocouple and a high-sensitivity (10-7V) electronic microvoltmeter G-1202.010. We found that the critical temperature of wettability for the system is at 1250K. We also observed that the wettability of 12Cr18Ni10Ti steel by the eutectic alloy of PbBi is significantly different in vacuum and in argon atmosphere, especially at high temperatures. It is therefore necessary to take the medium (vacuum, or inert gas and its pressure) into account when interpreting experimental data on critical temperatures of wettability.

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References


The alloys of the Pb-Bi-Li system are promising materials used in designing high efficiency thermonuclear energy reactors [1], which necessitates the study of their thermophysical properties. However, there are no published experimental studies on the temperature and composition dependence of surface tension (ST) of Pb-Bi-Li alloys [2,3]. To date, the phase diagram of the system is not fully built, with only fragmented data available on the proposed liquidus and solidus curves based on marginal eutectics of the Pb-Bi-Li system [4]. In the presented study the surface tension of the Pb-Bi-Li system was measured for the first time along the $\text{Pb}_{44.5}\text{Bi}_{55.5}$ eutectic. The ST was measured with a sessile drop method in the concentration range with up to 24.2 at. % content of Li and in the temperature range from the liquidus to 620K, with confidence errors of ~1%. The components Bi (99.9999%), Pb (99.9999%) and Li (99.9%) were melted in vacuum at $10^{-5}$ Pa, with the alloys thermally treated for at least 1 hour before each measurement. Based on the obtained experimental data we conclude that Li is a weak surface-active component in the $\text{Pb}_{44.5}\text{Bi}_{55.5}$ based alloys, which agrees with the basic criteria of surface activity in liquid metal alloys. We also estimated in MathCAD the adsorption of Li in the studied alloys using the Guggenheim-Adam (N-variant) method. We show that the maximum adsorption of Lithium in the $\text{Pb}_{44.5}\text{Bi}_{55.5}$ eutectic alloy is expected at the concentration of around 5 at. % Li.

Acknowledgment: This work was conducted with financial support from RFFI under Project N13-08-00121_a.

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The knowledge and the capacity to describe the vapour–liquid equilibria of systems composed of water and alcohols are crucial for the design of separation processes. In this work we present the study of the ternary system water+ethanol+1-propanol completing the cycle of previous studies [1-3]. For systems of this kind, the data is scarce and some obtained many years ago. With the resources that we have nowadays, more accurate data can be obtained. To obtain the experimental data of this ternary system we used a flow apparatus described in previous work [4]. The Cubic-Plus-Association equation of state (CPA EoS) [5] was used to predict the experimental results. This equation already showed to be able to properly describe the VLE of the binary systems constituting this ternary system, using a single, constant for all the alcohol systems and temperature independent binary interaction parameter. The information taken from the binary data CPA EoS prediction is here transferred for the ternary system phase equilibria description.

References

Theoretical Modeling of n-Alkane Adsorption on Different Porous Materials using the SAFT-FMT-DFT Approach

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In this work, a theoretical approach that combines elements of the statistical associating fluid theory (SAFT), fundamental measure theory (FMT), and classical density functional theory (DFT) to create a framework to model fluids in the presence of external fields. The SAFT-FMT-DFT approach is used to calculate single pore isotherms to develop a pore size distribution different porous materials, described by the 10-4-3 fluid-wall potential, based on nitrogen adsorption at 77 K. The pore size distribution is then used to predict excess adsorption isotherms for alkanes. The predicted isotherms are found to be in good agreement with the experimental data.
Lessons from the 2015 DOE Quadrennial Technology Review: The Role of Research and Development in our Energy Future

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The second Quadrennial Review, QTR 2015, is a comprehensive analysis of the state of the technologies to support the tremendous span of the Energy Enterprise in the US and around the world. The review includes systems analyses and technology assessments for Fuels and Feedstocks, Electric Power Systems, Modernization of the Electric Grid, Building Systems Efficiency, Industry and Manufacturing, Clean Transportation and Vehicle Systems, and Enabling Capabilities for Science and Energy. The report is supported by 60 in-depth technology assessments for the foundational technologies for these topical areas. The results of these analyses and the resulting set of opportunities, challenges, and priorities will be discussed.
We consider the $d$-dimensional imperfect (mean-field) Bose gas confined in a slit-like geometry and subject to periodic boundary conditions. Within an exact analytical treatment we first extract the bulk critical properties of the system at Bose-Einstein condensation and identify the bulk universality class to be the one of the classical $d$-dimensional spherical model. Subsequently we consider finite slit width $D$ and analyze the excess surface free energy and the related Casimir force acting between the slit boundaries. Above the bulk condensation temperature ($T > T_c$) the Casimir force decays exponentially as a function of $D$. For $T = T_c$ and for $T < T_c$ its decay is algebraic. The magnitude of the Casimir forces at $T_c$ and for $T < T_c$ is governed by the universal Casimir amplitudes. We extract the relevant values for different $d$ and compute the scaling functions describing the crossover between the critical and low-temperature asymptotics of the Casimir force. The scaling function is monotonous at any $d \in (2, 4)$ and becomes constant for $d > 4$ and $T \leq T_c$. 

Critical Casimir Forces Near Bose-Einstein Condensation of an Imperfect Bose Gas

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Colloids are ideal systems for investigating both spatial and temporal processes using optical methods since they have particle sizes larger than the characteristic size of atomic or molecular systems. We performed direct imaging experiments in order to investigate the concentration-driven non-equilibrium fluctuations in different nanocolloidal suspensions with a range of particle sizes and at different concentrations. We used a dynamic structure factor algorithm for image processing in order to compute the structure factor and to find the power law exponents and the correlation time of these fluctuations. The spatial-temporal evolution of fluctuations was also investigated and provides insight about correlation length and lifetime of fluctuations.
This presentation will focus on Tony Goodwin’s contributions to Schlumberger, an oilfield services provider. Tony’s career at Schlumberger encompassed over 15 years of work, during which he introduced his colleagues to the diverse set of techniques by which fluid properties are measured. In addition to his wide knowledge of fluid sensors, Tony also brought to Schlumberger the techniques by which serious, rigorous benchmarking of fluid sensors is performed. By applying these techniques we were able to determine which sensors performed best for the harsh environment found in an oil well. This talk will describe Tony’s impact on Schlumberger as well as his generosity in sharing his knowledge with me during my early days at Schlumberger.
In Memoriam: Anthony (Tony) Goodwin

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Anthony (Tony) Goodwin was a leading innovator in the field of thermophysics, and widely known as a researcher, author, and journal editor. Following his untimely death in December 2014, at the age of just 53, we review in this paper Tony’s outstanding contributions to the field of thermophysics and recount some of the personal qualities that his many friends and colleagues in the community will cherish.

Tony excelled as an experimentalist and devoted much energy to improving a variety of experimental techniques to facilitate measurements of thermophysical properties either under wider ranges of conditions, or with lower uncertainty. In a career spanning academia and industry, he worked on a number of key problems that presented both scientific challenges and opportunities for industrial application. We mention in particular his work on measurements of the speed of sound, relative permittivity, fluid phase behaviour, density and viscosity. In his industrial career, Tony was responsible for the development and testing of sensors for measuring many of these same properties for purposes of downhole fluid analysis in the petroleum industry. He published around 100 articles in the archival scientific journals, edited a number of books, authored or co-authored numerous chapters and was granted a large number of patents. He was also a powerful influence within the Physical Chemistry Division of IUPAC and the International Association of Chemical Thermodynamics. Drawing both on our personal experiences of collaborating with Tony and on his published work, this paper will highlight his lasting scientific achievements.
Polymers are often enhanced by nano-fillers, mainly in order to modify its optical and mechanical properties. Essentially by increasing the number of crystallites by adding heterogeneities, the product can be made optically transparent, stiff and reduce the production time by increasing the rate of crystallization. The same effect can be reached also by significant supercooling of the molten polymer. Then the homogeneous nucleation overrun the heterogeneous and end up with orders of magnitude finer structure. The comparison of these two crystal nucleation mechanisms and their interplay on example of poly (e-caprolactone) (PCL) was the aim of this study. In order to avoid crystallization on quenching to the temperature region of homogeneous nucleation, the cooling rates of 30,000 K/s should be realized for PCL, highly nucleated with multi-walled carbon nanotubes (MWCNT). The processes at such cooling rates can only be investigated by fast scanning chip calorimetry, which allows both cooling up to 10 MK/s, precise temperature profile realization with the accuracy of 1 ms and the quantitative heat capacity measurement. As soon as the sample is quenched, it crystallizes almost independently on the amount of the expensive nucleating agent, because of the large number of homogeneous nuclei. The observation is compared for different industrially important and bio- polymers: poly (butylene succinate) (PBSu), poly (butylene teraphtalate) (PBT) and poly (butylene naphtalate) (PBN). All show essentially the same effect, depending on the separation of homogeneous nucleation kinetics and crystal growth kinetics.
Thermophysical properties of liquid metallic alloys are important as input values for the numerical modelling of casting and solidification and for a better understanding of liquid properties related to the properties of the final cast product such as the glass forming ability of multicomponent metallic alloys. Measurements are complicated by high temperature and high chemical reactivity of many alloys in the liquid phase such as Ti- and Zr-based alloys. This problem can be overcome by containerless processing techniques based on electromagnetic levitation. Microgravity conditions are favourable or required for the measurement of the viscosity, fluid flow investigations,
quantitative non-contact calorimetry and for thermophysical property measurements in the undercooled liquid phase. An electromagnetic processing device has been installed on the International Space station with operations to start in 2015. Alloys to be investigated include Ni-based superalloys, Ti-alloys, generic Fe-alloys as model systems for high alloyed steels, and Zr- and Fe-based bulk metallic glass forming alloys. An overview over the planned experiments, experimental techniques will be given, preliminary results will be presented. Measurements on board the ISS are prepared by short duration microgravity experiments such as parabolic flights, by a ground based measurement programme and by modelling of fluid flow in electromagnetically levitated droplets including investigations of the onset of turbulence and the investigation of fluid flow effects on metastable phase formation and growth. Results of recent parabolic flight experiments will be presented including the surface tension of an FeCrNi alloy and of two γ-TiAl alloys.
Experimental Study on Vaporization Heat of Ethyl Fluoride (HFC161)

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The disadvantages of the traditional refrigerants on environmental protection and the difficulties in exploring the pure refrigerants make alternative refrigerant researchers focus their studies on HFCs mixtures. Among possible constituents of HFCs mixtures, Ethyl fluoride (HFC161) exhibits excellent environmental performance and usability. But the thermophysical properties data of HFC161 are reported rather rarely. The vaporization heat of liquid, which is widely used in energy, chemical engineering and other fields, is one of the most important thermophysical properties. Vaporization heat is also the indispensable data for scientific research and engineering design. However, the vaporization heat data of a large number of fluids had been obtained by means of difference between the enthalpy of the saturated vapor and that of the saturated liquid indirectly. In the present work, the vaporization heat data of HFC161 has been measured using a adiabatic calorimetric apparatus over the temperature range from (249.62 to 364.50)K, together with the vaporization heat of HFC134a measured in the temperature range from (284.88 to 340.95)K for verifying the experimental apparatus.

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Measurement of The Vapor Pressure and Critical Parameters of Ethyl fluoride (HFC161)

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Nowadays, many alternative refrigerants are studied for protecting ozonosphere. HFC161 is one of these refrigerants which are friendly to environment, because its ODP (Ozone Depleting Potentials) is zero. And it has a very low global warming potential, a high cooling capacity and an excellent energy efficiency. However, through literature review, the thermophysical properties data of HFC161 are reported rather rarely. The lack of data of properties restricts the development of related science research and engineering application. In present work, the vapor pressure of HFC161 has been measured using a static type apparatus over the temperature range from (233.15 to 375.15)K, together with the vapor pressure of isobutane (R600a) measured in the temperature range from (275.60 to 343.16)K for verifying the experimental apparatus. The measured vapor pressure data and data reported by other investigators have been evaluated, and a vapor pressure data set with reasonable accuracy has been obtained. Based on this consistent and reliable data set, a Wagner type equation has been proposed. This equation contains four coefficients and correlates the measured vapor pressures with high accuracy. The Critical parameters of HFC161 also been measured in this work. We acknowledge the support of the National Natural Science Foundation of China (Grant No.51276143).
An equation of state is presented for the thermodynamic properties of cold and supercooled water, based on the two-state model where liquid water is considered as a mixture of two different structures. The equation is valid for temperatures from the homogeneous ice nucleation temperature up to 300 K and for pressures up to 400 MPa, and can be extrapolated up to 1000 MPa. The equation of state is compared with experimental data for the density, expansion coefficient, isothermal compressibility, speed of sound, and heat capacity. In the range of validity, all experimental data that are considered reliable are represented within the experimental accuracy. The melting curve of ice I is calculated from the phase-equilibrium condition between the proposed equation and an existing equation of state for ice I.
Lignin is unique among biopolymers in having significant aromatic character, which makes it potentially attractive for a wide range of uses, including resins, coatings, and even carbon fibers. Unfortunately, most of the commercial-grade lignins available today (i.e., Kraft lignins) are severely limited in their applications because of their high metals (primarily sodium) content. We have discovered a powerful, versatile, and renewable mixed-solvent system that forms liquid-liquid phase behavior when contacted with lignin, such that the metals content of the lignin can be reduced 10-fold with each successive phase split. For example, lignin fractions containing 25ppm Na have been obtained from only two successive phase splits. Furthermore, this phase separation separates the lignin itself into lignin fractions of significantly different molecular weights, chemical compositions, and solvent content. The effect of processing temperatures and solvent feed composition on the solid-liquid to liquid-liquid phase transition, metals content, solvent content, and molecular properties of the lignin fractions isolated by our so-called ALPHA process have been measured. Implications of these results for the development of a commercially viable purification and fractionation process for lignin are also discussed.
On the Development of Direct Measurement Technique for Calorific Value of Natural Gas

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As an important non-renewable energy, natural gas plays a significant role in the development of national economy. Currently, the natural gas trading is mainly based on the volume measurement, which is not suitable and causes deviation when the composition of the natural gas varies. Therefore, numerous research works about the energy measurement of natural gas have been doing all over the world. Actually the major part of energy measurement is to accurately obtain the calorific value of natural gas. This paper introduces the development of direct measurement technology for calorific value, summarizes and analyzes the different direct measurement techniques. Meanwhile, based on the current status of calorific value measurement in our country, the direction of its development is indicated and the respective recommendations are made accordingly.
Reliable gas hydrate phase behavior predictions are critical to petroleum and natural gas processing and other gas processing equipment. Inaccurate predictions of gas hydrate phase equilibria can also lead to erroneous design of process facilities, which may lead to safety hazards and flow assurance issues, including plugging of flowlines. The most significant advancement of gas hydrate phase equilibrium predictions is based on the statistical thermodynamic approach, introduced by van der Waals and Platteeuw (vdWP) in 1959. Over the next several decades the vdWP model was extended to model gas hydrate formation in multicomponent mixtures. In addition, some of the simplifying constraints in the original model, such as accounting for multiple guest occupancy and guest–guest interactions, were dropped. Surprisingly, little attention was given to correct the fluid phase part of the model. For instance, limitations in the fluid phase models include not accounting for the effect of molecules showing hydrogen bonding and also electrolyte contributions, which may lead to significant errors in most of the gas hydrate forming systems containing polar hydrate formers, inhibitors, and salts. Predictions of gas hydrate phase equilibria for polar hydrate formers and inhibited systems in presence of salts like NaCl, KCl, CaCl2, and also methanol, ethanol, monoethylene glycol, are critically important to flow assurance and operation. Unfortunately, the currently in use models show large errors in the fluid phase equilibrium predictions and since these models are inherently connected to the gas hydrate model, the overall gas hydrate phase equilibrium predictions are negatively affected. In particular, this is the case due to the following limitations: (1) the availability of vapor-liquid equilibria data for high salt concentrations, (2) appropriate electrolyte models (3) an equation of state accounting for association. To overcome these limitations, this work reviews and implements various fluid phase equilibrium models for improved predictive capabilities for a range of hydrocarbons, from low to higher molecular weight, polar components, organic inhibitors and electrolytes.
Physicochemical Properties of SnZn Eutectic with addition Al, Ag and Li

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Surface tension and density of liquid has been studied as a function of composition and temperature. Melting temperature was determined by DSC. Linear thermal expansion and electrical resistivity we studied. The effect of alloying additions of the tensile properties was determined. Microstructure of as-cast alloys was studied by means of scanning electron microscopy and phase composition by means of XRD.
Exhibit Table
Exhibit Table
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Exhibit table.
Presentation of the 2015 Symposium Award

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Presentation of the 2015 Symposium Award