

Fitting Helmholtz Energy Equations of State through a Combination of Experimental Data and Values Obtained with Molecular Simulations

Monika Thol^{C, S}

Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, Bochum, Germany

m.thol@thermo.rub.de

Gábor Rutkai, Andreas Köester and Jadran Vrabec

Lehrstuhl für Thermodynamik und Energietechnik, Universität Paderborn, Paderborn, Germany

Roland Span

Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, Bochum, Germany

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.