Speed of Sound of Siloxanes from Experiment and Molecular Simulation

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Today, almost every effort that aims at technological process design and optimization requires a sufficient amount of reliable thermodynamic data for the involved fluids. Traditionally, thermodynamic properties are obtained from experiments and are subsequently expressed in terms of equations of state (EOS). In heat recovery systems, such as organic Rankine cycles (ORC), one important group of ORC working fluids are the siloxanes, which belong to the wider class of organo-silicone compounds. In particular, hexamethyldisiloxane (HMDS) appears to be an eligible candidate for becoming a widely used working fluid for high-temperature ORC processes. However, the current lack of accurate thermo-physical data for siloxanes may lead to sub-optimally designed cycles and processes.

This work aims to satisfy the need for raw thermodynamic data including the speed of sound for HMDS. The presented data were obtained from both experiment and molecular simulation. Recent progress in molecular simulation has shown that molecular models (force fields) have powerful predictive capabilities with respect to thermodynamic data [3]. Such information can also be straightforwardly accessed for fluids and states which are experimentally difficult to investigate. Thermal properties in the homogeneous fluid region, together with the speed of sound and the vapor pressure are used to generate accurate equations of state (EOS) that describe the entire range of fluid states. Nowadays, it is acknowledged that "*properly designed multiparameter equations of state are able to represent thermodynamic properties of a certain substance within the accuracy of the most accurate experimental data*" [2]. The measurement mechanism of the apparatus employed in this work is based on the puls-echo technique and operates up to 150 MPa in the temperature range between 250 and 600 K [1]. While emitting a high frequency modulated burst signal by a piezoelectric quartz crystal, which is positioned between two reflectors in the fluid, the speed of sound is determined by the traveled distance divided by the signal propagation time. Simulation results were obtained by the molecular simulation tool *ms*2 [4], covering a large part of the technologically relevant part of the homogeneous fluid region. In addition to the speed of sound, the molecular simulation data set contains numerous other thermodynamic properties including temperature, density, pressure, residual isochoric and isobaric heat capacity as well as residual internal energy.

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