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EQUATION OF STATE MODELING AND MOLECULAR SIMULATION OF FLUIDS WITH POLAR INTERACTIONS

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ABSTRACT

The thermodynamic behavior of many fluids is significantly influenced by polar interactions. Molecular-based equation of state (EOS) models describe the Helmholtz energy of fluids based on perturbation theory and account for polar contributions by an additive term. In this work, polar contribution models have been comprehensively evaluated and compared for the first time. Both dipole contribution models and quadrupole interaction models were studied. Therefore, molecular simulations of simple polar model fluids were carried out to establish a database of reference data. The evaluation of the polar models was conducted using model fluids, which consist of a 12-6 Lennard-Jones (LJ) interaction site with a point multipole, i.e. either point dipole or point quadrupole. As the kernel, the LJ EOS of Kolafa and Nezbeda [1] was used in all cases, which is known to describe the LJ fluid very well [2]. A large range of dipole moments and quadrupole moments were studied. Important differences for the different polar models were obtained. Molecular simulations were used to determine pseudo-experimental data, which provide a robust basis for testing the theories. In this study, as shown in Figure 1, a large set of reference data was used to validate the accuracy of the polar contribution, obtained through molecular dynamics (MD) and Monte Carlo (MC) simulations using the ms2 [3] simulation engine. In the simulations, both homogeneous states and vapor-liquid equilibria (VLE) were studied. Additionally, Brown's characteristic curves [4] were determined using a simulation method developed in a previous work of our group [5]. Brown's curves are a tool for the assessment of the extrapolation behavior of thermodynamic models.

The VLE data are described well by most of the studied polar EOS models. However, for homogeneous state points, significant deviations between the data from computer experiments and some EOS models were obtained for many properties. These deviations increase with increasing polar moment, as expected. Most importantly, all studied polar contribution models yield some critical artifacts. Thus, robust new polar contribution models are required. We discuss possible paths for developing such models based on the comprehensive study carried out here.

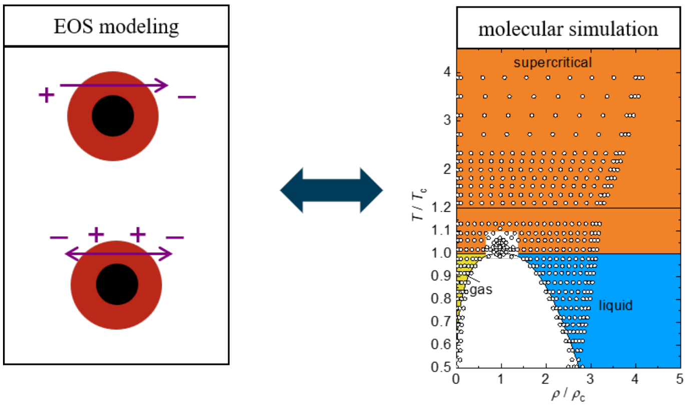

Figure 1: Schematic representation of comparison of the equation of state modeling with reference data obtained from molecular simulations.

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