A Theoretically Based Departure Function for Multi-Fluid Models

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The state-of-the-art in accurate mixture modeling is the multi-fluid model formulated in the reduced Helmholtz energy, see, e.g. [1]. The model consists of an ideal part and a residual part. The residual part is again split in two parts: a sum over all residual reduced Helmholtz energies of the pure fluids times the respective mole fractions and the so-called departure function. Omitting the departure function, the model contains four adjustable parameters, namely β_v, β_T, γ_v, and γ_T, which can be fitted to experimental data or which can be set to some specific values in order to obtain predictive standard mixing rules. So far, the departure function cannot be used in a predictive manner, because its structure is not known a priori but has to be determined in a fitting procedure by mainly trial and error. In this work, we propose a new theoretically based departure function for multi-fluid models. The new formulation makes use of the well-established idea of combining equations of state with excess Gibbs energy models, see, e.g. [2]. The multi-fluid model was combined with the UNIFAC [3] model. In order to demonstrate the capabilities of the new model, calculated phase equilibria for all binary mixtures of the components CO_2, ethane, propylene, benzene, and ethanol have been compared to experimental data. The representation of phase equilibria for all of these binary mixtures is improved compared to the multi-fluid model with standard mixing rules. Furthermore, it is shown that standard mixing rules fail to predict azeotropic behavior of the considered mixtures, while the new model is capable of describing these mixtures well.

References:

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