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Quantitative Prediction of Thermodynamic Properties and Phase Equilibria based on first-order Perturbation Theory

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Thermodynamic Perturbation Theory (TPT) provides a powerful framework for predicting the thermodynamic properties, structure, and phase equilibria of fluids. A difficulty associated with TPT-based models is that the high accuracy demanded by typical engineering applications requires higher-order perturbation terms to be considered in the perturbation expansion. Already for simple Van-der-Waals fluids one needs to include at least up to the third-order perturbation term to obtain an accurate description of vapour-liquid equilibria to within reasonable distance from the critical point. The same holds for the description of thermodynamic properties at low density or temperature, and the description of higher-order derivative properties such as heat capacities. Though the first-order perturbation term is relatively easy to calculate, the computation of higher-order terms is generally not straightforward, especially if one wishes to go beyond simple spherical molecular models to more complex molecular shapes. Additionally, for the description of higher-order perturbation terms of fluid mixtures one normally has to rely on approximations suggested by the mathematical form of the first-order perturbation term, which are not guaranteed to be accurate. Examples are Van-der-Waals one-fluid theories, and approaches that assume all perturbation terms can be written as a double sum over molecular pair-interactions. In this work we develop an alternative to adding higher-order perturbation contributions for improving the accuracy of an equation-of-state model. Our approach is based solely on first-order perturbation theory and, at least for fluids whose molecules interact by a Mie $m-6$ potential, we show it surpasses any of the most accurate (molecular-based) equations of state up to date. Given the approach is based on first-order perturbation theory it allows a more natural extension to mixtures, which is shown to result in an improved description of binary phase equilibria as compared to any higher-order theory.