

Extrapolation to an Infinite-Order Perturbation Theory

Ahmad F. Ghobadi and J. Richard Elliott^{C,S}

Chemical Engineering Dept., The University of Akron, Akron, OH, U.S.A.

dickelliott@uakron.edu

In recent work, we characterized the repulsive and attractive contributions to the Helmholtz energy of realistic molecular fluids via adaptation of a third-order Weeks-Chandler-Andersen (WCA) perturbation theory [Ghobadi and Elliott, *J. Chem. Phys.* 139, 234104 (2013)]. In the process, fused soft chains of varying length were simulated interacting with WCA potential at several densities and temperatures, covering the entire phase diagram. Perturbation contributions were computed using the configurations of the purely repulsive reference term. The resulting EOS, referred to as the SAFT- γ WCA EOS, provided accurate agreement with the thermophysical properties of pure fluids and mixtures. Consistent with the findings of Avendano et al [J. Phys. Chem. B 115, 11154 (2011) and J. Phys. Chem. B 117, 2717 (2013)], the inclusion of the third-order perturbation term substantially improved the predictions of the EOS in the critical region. Furthermore, it appears that the third-order term can be correlated by scaling the second-order term with a Gaussian function. In this work, we assume that the higher-order perturbation terms follow the same trend and test two methods for resumming the series to infinite order. From a physical perspective, this renormalization function incorporates the impact of the long-range density fluctuations on the thermophysical properties. We demonstrate that one can obtain a remarkable agreement with experimental critical pressure, temperature, and density without sacrificing accuracy outside the critical region. To capture anomalies of derivative properties such as heat capacity at the critical point, we augment the extrapolated TPT EOS with a correction term, originally proposed by Span and Wagner [J. Phys. Chem. Ref. Data 25, 1509 (1996)]. Similar to the Span Wagner application, the extrapolated EOS is very close in the critical region and the augmented term focuses on the non-classical correction. We show how the non-classical correction can be generalized to apply to a range of hydrocarbons. The extrapolation procedure can also be applied to other implementations of perturbation theory. We provide an application to the PC-SAFT EOS to support the generality of the proposed scheme. Comparing to the procedures that are based on Renormalization Group (RG) Theory, application of the G-function is simpler and less computationally expensive. It requires no iteration on the Helmholtz free energy and does not involve numerical integration or differentiation. The extension to mixtures and long-chain molecules is also carried out in a straightforward way without sacrificing the accuracy or introducing additional adjustable parameters. With this approach, perturbation theory can provide accuracy that is competitive with multiparameter equations in the critical region.