276d Extrapolating Molecular Models of Thermodynamic Properties to Polymeric Species

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Molecular simulation of truly polymeric species is not feasible with current computers, nor would it be reasonably efficient even if it was feasible. Generally, simulations are performed for a few oligomers and the thermodynamics are assumed to follow the behavior of the largest oligomer simulated, without rigorously analyzing the convergence of trends with increasing molecular weight. Many theories simply assert that chain molecular properties scale linearly with molecular weight for all chain lengths. A particular example is the Statistical Associating Fluid Theory (SAFT). In the SAFT model, the molecules are assumed to be chains of freely jointed spherical segments which have both hard chain and dispersion behavior. Variations on the original model include the SAFT-VR and PC-SAFT models. The relations of the number of segments to the number of carbons and details of the higher order attractive perturbation contributions vary substantially between implementations because these are tuned to experimental data rather than simulation data and cancellations of errors between the repulsive and attractive contributions mask the true underlying behavior.

In this study, we compare the SAFT assumptions with asymptotic trends of thermodynamic perturbation terms based on Step Potential Equilibria and Dynamics (SPEAD) model for n-alkanes. The perturbation terms are characterized in terms of the Helmholtz energy as A0, for the repulsive reference fluid, A1 for the first order attractive perturbation, and A2 for the second order attractive perturbation. The n-alkanes showed that asymptotic behavior was approached by C20 for the A0 and A1 contributions, but the asymptote was not approached until C80 for the A2 term. We found qualitative agreement with the SAFT/TPT1 formulation for the A0 and A1 terms, but the A2 contribution is qualitatively different. Applying the TPT2 correction improves the agreement with the A0 term, but does not affect A1 or A2 significantly. We attribute most of the difference in A2 to application of the microscopic compressibility approximation for PC-SAFT and to the linear assumption for other implementations.

We also extend the trend analysis to branched alkenes representative of cis-1,4-polyisoprene (natural rubber). To characterize the polymer we simulated the monomer (C5) through the 8mer (C40) of cis-1,4-polyisoprene, and compare to trends of the n-alkanes with comparable molecular weight. This leads to identification of effective segment numbers for application with the n-alkane trend for A0 and A1, but there is a qualitative difference in the trend for A2 of the branched compounds. This difference may be attributed to distinction in the fluctuation behavior, to which A2 is most sensitive. We test the analysis using recently obtained experimental data for extraction of natural rubber with an expanded liquid of CO2+propane. This procedure demonstrates one rigorous procedure for extrapolating to polymer thermodynamics while maintaining the detailed distinctions between components at the molecular level.