

Discontinuous Molecular Simulations for Computing Excess Entropy of Polymer Solutions

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ABSTRACT

Polymeric mixtures of hydrocarbons, alcohols have been simulated with discontinuous potential models to characterize the Helmholtz energy of the repulsive reference fluids (A0) along with the first and second order perturbation contributions (A1, A2) as functions of density and composition. Taken together, these terms generate a complete equation of state for the mixture, including temperature effects as well as density and composition. The specific hydrocarbons studied were methane, ethane, propane, n-butane, n-hexane, n-heptane, n-decane, and benzene. The specific alcohols were water, methanol, ethanol, n-propanol, and n-octanol. Unfortunately, a slight inconsistency was encountered when the trend observed for these small molecules was extrapolated to the long chain limit. Therefore, we extend the analysis to mixtures of n-alkanes, branched hydrocarbons, and aromatics with polymeric molecules of: n-alkanes, ethyl-styrenes, ethyl-propylenes, and isoprenes. The perturbation contributions can be accurately characterized by van der Waals mixing rules. Candidates for the interpolation model included the NRTL and Wilson models as well, but the simpler van der Waals model proved quite reliable for characterizing the trends in excess properties with respect to composition. Associative contributions to the Helmholtz energy were attributed to Wertheim's theory in developing the molecular models of the alcohols but were not the object of study in the present investigation. Noting that the Helmholtz energy for the reference contribution is simply related to the athermal entropy, we find that the athermal entropy of mixing deviates significantly from ideality, but still follows the van der Waals mixing formula. This leads to an accurate characterization of the entropic contribution to the chi parameter of Flory-Huggins theory for mixtures of all sizes and shapes. A general rule is developed for predicting the athermal entropy of mixing based on knowledge of the volume ratios of the constituent molecules. Combined with the usual approach to characterizing the energetic contribution to the chi parameter, a complete formulation is provided for characterizing the mixture thermodynamics. A general rule is developed for predicting the athermal entropy of mixing based on knowledge of the volume ratios of the constituent molecules. The simulations are compared to several theories, including the MCSL theory for hard spheres, the SAFT model, and the Guggenheim-Staverman theory. Finally, discontinuous Monte-Carlo and Molecular Dynamics methods have been performed to show the ergodicity phenomena in our systems and effect of coarse-graining simulations has been discussed. Keywords: Physical properties, molecular simulation, Henry's Law, density, phase equilibria