Development of a Universal m-6-8 United Atom Force Field for Accurate Molecular Simulations

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Simulation methods for virtually any thermophysical property for any material have been developed and well-documented in the literature. However, the accuracy of chemical simulations is limited by the accuracy and transferability of the intermolecular force models used in the computations. The majority of current force fields are effective two-body potential models of the Lennard-Jones 12-6 form with parameters optimized for a subset of properties (density, heat of vaporization, phase equilibria, etc.) and usually for a subset of compounds (hydrocarbons, alcohols, proteins, etc.). Unfortunately, when those effective potential parameters are used for other properties or compounds, the accuracy of the simulations decreases.

Recently we have shown that adjusting the repulsive wall of the potential and including an additional term in the dispersion series improves the predictive capabilities of molecular-scale simulation. United atom site parameters for the so called “m-6-8” potential have been optimized using second and third virial coefficient data for ethane, n-butane, isobutane, and neopentane. The resulting force field was then used to predict second and third virial coefficients, gas phase viscosities, and phase equilibria of small to medium linear and branched alkanes. Further improvements in the prediction of phase equilibria and third virials were obtained by adding a three-body, Axilrod-Teller triple-dipole dispersion potential to the calculations.

In this paper we will detail the parameters and simulation results obtained in this study and present comparisons with other simulation force fields. In addition, we will present results illustrating the effect of three-body forces on the prediction of critical points in hydrocarbons using UA site-site potentials.