Beyond united-atom Lennard-Jones: Reliable prediction of high pressure viscosities

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ABSTRACT

Accurate prediction of viscosity (η) at high pressures (P) necessitates an extremely reliable force field for at least two reasons. First, the viscosity at a given density (ρ) is highly sensitive to the function form and associated parameters, especially those of the non-bonded interactions. Second, the viscosity depends strongly on the predicted density, which is also very sensitive to the force field.

As preliminary work suggests that traditional united-atom Lennard-Jones n-6 force fields are not capable of accurately predicting high pressure viscosities, a novel anisotropic-united-atom model is proposed. To develop a highly accurate force field, the CH_3, CH_2, CH, and C non-bonded parameters are optimized simultaneously using a large data set, consisting of $P\rho T$ and caloric properties over a wide range of state points, with particular emphasis at high pressures, for several normal and branched alkanes. Since the challenge compound is 2,2,4-trimethylhexane (TMH), we use 2,2,4-trimethylpentane (TMP, a.k.a. isooctane) as a surrogate molecule to refine the non-bonded parameters and, consequentially, to improve transferability.

An essential aspect of the challenge is to provide meaningful estimates of uncertainty. For this reason, uncertainties in the predicted TMH viscosity are quantified using three different methods. First, we estimate systematic bias in the force field by comparing the simulated and REFPROP η values for the surrogate compound, TMP, at the challenge temperature and pressures. Second, we account for the uncertainty in η that is associated with uncertainties in ρ for a given P. Third, we implement Bayesian inference to quantify and propagate the uncertainty in the force field non-bonded parameters.