High pressure simulations to infer the repulsive barrier of the Mie n-6 non-bonded potential

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ABSTRACT

Outline:

1. Mie potential where the repulsive exponent is a fitting parameter provides increased accuracy for VLE
2. However, there is concern over the theoretical justification of using a harder repulsive exponent
3. This study tests the Mie potential at higher pressures where the close-range repulsive interactions become more significant
4. This is achieved by rigorously quantifying the uncertainty in the non-bonded parameters and propagating those uncertainties when predicting compressed liquids
5. A comparison is made between the Mie and Exp-6 potentials

Over the past decade, the Mie n-6 (generalized Lennard-Jones) non-bonded potential has provided significant improvement when predicting vapor-liquid equilibria (VLE) properties of organic compounds. The optimal value of n is typically greater than 12 for a united-atom (UA) force field optimized with VLE data (e.g. $n_{\text{TAMie}} = 14$ or $n_{\text{Potoff}} = 16$). However, there exist strong theoretical concerns that $n/ge12$ is too repulsive at short distances. While the forces at close-range distances do not dramatically impact VLE properties, they can play a large role at high pressures.

For this reason, we investigate the practical implications of using a Mie n-6 potential for $n \geq 12$ at high pressures. Specifically, we determine if the UA Mie n-6 accurately predicts the compressibility factor (Z) and viscosity (η) of normal and branched alkanes at high pressures. We observe a large positive bias in Z and η for $n > 12$ at high pressures that increases with increasing n. Bayesian inference of the non-bonded parameters demonstrates that no set of ε, σ, and n adequately predicts both VLE and high pressure properties. Also, we do not observe any improvement when comparing the Mie n-6 results with those of the Buckingham exponential-6 potential, which is purported to have a more realistic repulsive barrier. These observations are of both practical and theoretical significance when selecting the non-bonded function form.