

Bayesian inference demonstrates inadequacies of Mie n -6 repulsive barrier at high pressures

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ABSTRACT

Over the past decade, the Mie n -6 (generalized Lennard-Jones, LJ) non-bonded potential has provided significant improvement when predicting vapor-liquid equilibria (VLE) properties of organic compounds. For united-atom (UA) force fields parameterized with VLE data, the optimal value of n is typically greater than 12, in contrast to the traditional LJ 12-6. However, there exist strong theoretical concerns that $n \geq 12$ 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 “best” function form for computing non-bonded interactions.