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

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ABSTRACT

Jadran, I have included outlines for two different proposals. The first proposal is to use more realistic nonbonded potentials to improve the high pressure extrapolation. The second proposal is to move beyond the Lorentz-Berthelot combining rules to improve the prediction of mixture properties. I would appreciate your insight regarding which of these is more likely to be funded and which is more important and/or interesting.

1 Outline: Need for more accurate nonbonded potentials

1. Background for hybrid data sets
   - (a) Design of efficient and reliable chemical processes requires accurate equations of state over a wide range of temperatures and pressures
   - (b) The quantity and quality of experimental data is insufficient for most compounds
   - (c) Molecular simulation is an ideal approach for overcoming the data deficiency at extreme temperatures and pressures
   - (d) Improved EOS are developed by supplementing experimental data with simulation results
2. Reliability of hybrid data set approach depends on accuracy of force field, specifically, how well the model extrapolates to extreme temperatures and pressures
   - (a) Recent work has demonstrated that the united-atom Lennard-Jones n-6 force field does not extrapolate from vapor-liquid equilibria to elevated pressures
   - (b) Improved extrapolation requires a more physically realistic nonbonded potential, e.g. an extended Lennard-Jones (12-10-8-6) potential
3. More sophisticated nonbonded potentials require higher dimensional parameterization
   - (a) Multistate Bennett Acceptance Ratio (MBAR) combined with basis functions (BF) has been shown to greatly accelerate force field parameterization
   - (b) MBAR reweights configurations sampled with a reference force field to predict energies and pressures for a non-simulated force field
   - (c) Basis functions store the energy and pressure contributions from the r^{-m} terms, where m are integer values such as 12, 10, 8, and 6
4. The combined MBAR-BF approach allows for iterative optimization of force field parameters to ensure internal consistency of derivative properties

2 Outline: Hybrid data sets for mixtures

1. Background for hybrid data sets
   (a) Design of efficient and reliable chemical processes requires accurate equations of state over a wide range of temperatures and pressures
   (b) The quantity and quality of experimental data is insufficient for most mixtures
   (c) Molecular simulation can supplement experimental data when developing mixing rules
2. Reliability of hybrid data set approach depends on accuracy of force field, specifically, the nonbonded cross interactions
   (a) Lorentz-Berthelot combining rules are common but not infallible
   (b) Alternative combining rules have not been tested extensively
   (c) Explicitly parameterizing the cross interactions should improve performance
3. Including cross interactions as fitting parameters requires higher dimensional parameterization
   (a) Multistate Bennett Acceptance Ratio (MBAR) combined with basis functions (BF) has been shown to greatly accelerate force field parameterization
   (b) MBAR reweights configurations sampled with a reference force field to predict energies and pressures for a non-simulated force field
   (c) Basis functions store the energy and pressure contributions from the r^{-m} terms, where m are integer values such as 12, 10, 8, and 6

3 Justification for funding

1. Why is this important?
   (a) Reliable estimates of thermophysical properties are of practical industrial importance
2. Why me?
   (a) Expertise in force field parameterization with MBAR-BF
3. Several novelties to expand my research horizon:
   (a) EOS development
   (b) Hybrid data set approach
4. Why Jadran?
   (a) Dr. Vrabec has helped pioneer the EOS hybrid data set approach
   (b) Substantial computational resources at disposal