Bayesian inference analysis of transferable, united-atom, Mie λ-6 force fields for normal and branched alkanes

Richard A. Messerly[1, a)]

Thermodynamics Research Center, National Institute of Standards and Technology, Boulder, Colorado, 80305

Keywords: Transferability, Force Field, Molecular Dynamics, Molecular Simulation

a) Electronic mail: richard.messerly@nist.gov

PURPOSE

The aim of this study is to demonstrate, with Bayesian inference, that a Mie potential cannot adequately predict VLE and compressed liquid pressures for alkanes. We then use simple Bayes factors (if not RJMC) to determine the optimal value of lambda for predicting compressed liquid pressures. For adequate prediction of VLE and compressed liquid pressures, we recommend using AUA models or perhaps Exp-6 or extended Lennard-Jones, i.e. 12-10-8-6.

OUTLINE

1. Introduction
2. Simulation details
3. Force field
4. Case Study for alkanes, show TraPPE and Mie (perhaps I could show the AUA models here as well)
5. Bayesian Theory
   (a) Posterior
   (b) MCMC
   (c) RJMC
6. MBAR as surrogate model
7. Higher pressure PoU
8. Different values of lambda cannot reconcile (already done for ethane, probably need to do for other alkanes)
9. AUA, AUA Mie, Exp-6

DETAILED OUTLINE

I. INTRODUCTION

1. Mie potential has received significant attention for its ability to predict VLE without requiring an all-atom representation

2. Reliable predictions for high pressure systems are important but have not been tested using the Mie potential

II. SIMULATION DETAILS

1. Perform NVT simulations in GROMACS

2. ITIC used to convert Udep and Z to rhol and Pvsat

III. FORCE FIELD

1. United-atom representation of alkanes (CH3, CH2, CH, and C sites)

2. Mie potential and Lennard-Jones potential (maybe include Exp-6 and extended Lennard-Jones, i.e. 12-10-8-6)

IV. CASE STUDY FOR ALKANES

1. Several force fields in the literature have been optimized to agree with VLE properties (TraPPE, Potoff, TraPPE-2, TAMie, Errington)

2. PVT trends are inaccurate for both TraPPE and Potoff at high pressures

3. 12-6 under predicts while 16-6 over predicts

4. However, since TraPPE and Potoff use slightly different objective functions we want to perform an equivalent analysis for different values of lambda

5. Hypothesis that we want to test is whether there exists a value of lambda that provides reasonable VLE and supersatured (however, for ethane this is not feasible)

6. AUA LJ 12-6 is much more accurate for ethane

7. AUA Mie 14-6 potential is not much better than UA Mie 16-6

8. AUA Exp-6 force field is not much better than UA Mie 16-6

V. BAYESIAN ANALYSIS

1. Rigorous approach to determine that the 16-6 is inadequate for reproducing VLE and compressed liquid pressures

2. Posterior includes saturated liquid density and vapor pressure

3. Markov Chain Monte Carlo is used to sample

4. Uncertainty is propagated for pressures

5. Determine optimal value of lambda for compressed liquid pressures by modifying posterior to include only saturated liquid density and compressed liquid pressures

VI. SURROGATE MODEL

1. MBAR is used to predict Udep and Z

2. ITIC is used to convert Udep and Z to rhol and Pvsat

3. ITIC state points are fit to rectilinear and antoine equation to interpolate rhol and Pvsat

4. Uncertainties in analysis are included in posterior

5. Very conservative estimates of uncertainty

VII. PROPAGATION OF UNCERTAINTY

1. The 16-6 potential is not able to predict both VLE and compressed liquid pressures

2. Repeat this process for 14-6 and 15-6

3. VLE is much worse for 14-6, about the same for 15-6

4. Condensed liquid pressures are slightly better for 14-6 and 15-6 but still over predict

VIII. FUTURE WORK

1. Show that the AUA LJ model is much more reliable, even more so than the AUA Exp-6 and AUA Mie. This must have to do with the larger shifted value.

2. At higher pressures you need the hydrogens, the higher the shift the better.

3. Alternative method is to use an extended Lennard-Jones potential, 12-10-8-6, that has the flexibility of a Mie potential but without the steep barrier