The role of force field uncertainty in the prediction of high pressure viscosities.

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ABSTRACT

Key points

Force field parameter uncertainty is negligible compared to Green-Kubo uncertainty We quantify both Mie and torsional uncertainties

Outline

1 Introduction

1. Introduce the industrial fluid properties simulation challenge
2. Discuss the details of the 10th challenge
3. Explain why this challenge is important/interesting:
   (a) Viscosity is an important property for designing chemical systems
   (b) Viscosity data typically do not cover the entire range of $P\rho T$ of interest
   (c) Prediction methods are typically quite poor for viscosity
   (d) Molecular simulation is an attractive alternative, but two main challenges
      i. Difficulty of obtaining reproducible results from simulation
      ii. Unreliable force fields
4. We performed a systematic investigation of several united-atom force fields and determined Potoff to be the most reliable
5. Although Potoff over predicts viscosity and pressure with respect to density, it is quite reliable at predicting viscosity with respect to pressure
6. The uncertainty in force field parameters is key for rigorously quantifying the uncertainty

2 Methods

2.1 Simulation set-up

1. NPT performed for each replicate such that a distribution of box sizes is obtained
2. Depending on the system, a simulation of 1, 2, 4, 8, 16, or 32 ns was used for the production stage
3. Details are in supporting information

2.2 Data analysis

Refer to Zhang, Best Practices, and Special Issue manuscript

1. Use 40% sigma for cut-off
2. Fit sigma to power model
3. Fit viscosity to double exponential
4. Bootstrap uncertainties by resampling replicate simulations
5. 12 time origins

2.3 Force fields

Copy the majority of this section from a previous publication

1. Potoff force field proved to be most reliable in previous study
2. United-atom, Mie 16-6
3. AUA4m considered modifying torsional barriers for CH_2-CH_2 by 15 % and 40 % for internal and terminal torsions, respectively.
4. Include uncertainty in ε, σ, and U^{tors}
5. Plots of MCMC samples and maybe the Mie potentials and torsional barriers explicitly

3 Results

1. Potoff results
2. Mie uncertainties are negligible
3. Torsional uncertainties are negligible
4. Mie and torsional uncertainties are negligible
5. Report estimated pressure coefficient

Figures:

1. Viscosity vs pressure
2. Bootstrap uncertainties
3. Validation of bootstrap approach for ethane?
4. Convergence of Green-Kubo plateau for 1000 MPa

4 Discussion/Limitations

1. Discussion
   (a) Branched alkanes are not as accurate, perhaps assumption of transferability or torsional parameters
   (b) Force field parameter uncertainties are not as significant as often perceived
   (c) Fixed bond lengths, 1.4 nm cut-off with tail corrections, 400 molecules, were all validated previously
2. Limitations
   (a) Largest viscosity simulations are slow to converge and unclear if simulations are sufficiently long
   (b) Tail-corrections could impact dynamics
   (c) Finite size effects

5 Conclusions

6 Acknowledgments

7 Supporting Information

7.1 Gromacs input files

1. Include all the .gro files
2. Include all the .top file templates
3. Include .mdp files
4. Or we can just include an example and then refer them to the GitHub website

7.2 Tabulated values

7.3 Green-Kubo plateau plots

7.4 Bayesian bootstrap analysis

Example analysis, i.e., bootstrap distribution, replicates