Humboldt Research Fellowship

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ABSTRACT

Key points

Mie and TAMie potentials are much better at saturation viscosities, despite not being fit directly to them Viscosity density curve is much harder to reproduce Viscosity pressure is adequately predicted with Potoff and TAMie Branched alkanes have slightly worse performance

Propane is accurate to nearly 1 GPa Butane agrees more closely with newer REFPROP correlation C12 has similar results for Potoff and TraPPE?

Entropy scaling for isooctane?

Wrong torsional parameters for some isocompounds?

Outline

1 Introduction

1. Viscosity is an important property for designing chemical systems

2. Viscosity data typically do not cover the entire range of $P\rho T$ of interest

3. Prediction methods are typically quite poor for viscosity

4. Molecular simulation is an attractive alternative, but two main challenges

    (a) Difficulty of obtaining reproducible results from simulation
    (b) Unreliable force fields

5. This manuscript applies the recent Best Practices to improve reproducibility such that it is possible to elucidate the difference in force fields

6. Previous studies have suggested that UA models may be inadequate, while Gordon showed that a Mie potential could accomplish both VLE and viscosity

7. This study tests whether the modern Mie potentials that are optimized for saturation thermodynamic properties are transferable to transport properties, e.g. shear viscosity

2 Methods

2.1 Force fields

Copy the majority of this section from a previous publication

1. United-atom and AUA models are the focus

2. LJ 12-6 and Mie n-6

3. Four force fields (although some have slightly different ethane parameters)

4. None of these force fields specify bond types, so we used fixed bonds

5. Torsions are the same for each force field

2.2 Simulation set-up

1. Two types of simulations performed, saturation and 293 K for compressed systems

2. Saturation simulations use the REFPROP densities such that, in some cases, the force field is actually in a metastable state

3. Performed some simulations at reported saturation conditions

4. NPT performed for each replicate such that a distribution of box sizes is obtained

5. Depending on the system, a simulation of 1, 2, 4, or 8 ns was used for the production stage

6. Details are in supporting information

2.3 Data analysis

Refer to Best Practices document

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

We have tried to

3 Results

3.1 Saturated Liquid

3.1.1 n-Alkanes

1. Ethane is exception where Mie potential significantly over-predicts viscosity

2. Propane, butane, n-octane all see significant improvement with Mie and TAMie

3. C12 has spurious results

Figures:

1. All n-alkanes together

3.1.2 Branched alkanes

1. Mie potential provides less improvement in these cases

Figures:

1. Pair a few together

3.2 High pressure fluid

3.2.1 n-Alkanes

1. Propane has accurate viscosity-P but not viscosity-rho
2. Butane appears to agree more closely with recent REFPROP correlation

Figures:

1. Propane $\eta - \rho$ $\eta - P$
2. Butane $\eta - \rho$ $\eta - P$
3. n-Octane $\eta - \rho$ $\eta - P$
4. n-Dodecane $\eta - \rho$ $\eta - P$?

3.2.2 Branched alkanes

1. Similar to n-alkanes?
2. Wrong torsions matters?

Figures:

1. Isobutane $\eta - \rho$ $\eta - P$
2. Isopentane $\eta - \rho$ $\eta - P$
3. Isohexane $\eta - \rho$ $\eta - P$?
4. Isooctane $\eta - \rho$ $\eta - P$
5. Neopentane $\eta - \rho$ $\eta - P$?
6. 3-methylpentane $\eta - \rho$ $\eta - P$?
7. 2,3-dimethylbutane $\eta - \rho$ $\eta - P$?

4 Discussion/Limitations

1. Discussion

   (a) Mie potentials parameterized with VLE data provide significant improvement over LJ 12-6
   (b) Potoff over-predicts $\eta - \rho$ dependence while TAMie is fairly accurate
   (c) Potoff appears to be slightly more accurate for $\eta - P$

(d) Branched alkanes are not as accurate, perhaps assumption of transferability or torsional parameters

2. Limitations

   (a) Largest viscosity simulations are slow to converge and unclear if simulations are sufficiently long
   (b) Tail-corrections could impact dynamics
   (c) Using REFPROP saturation conditions instead of force fields

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

1. Ethane

   (a) Saturation
       i. Potoff
       ii. TraPPE
       iii. AUA4
       iv. TAMie
   (b) T293 highP
       i. Potoff
       ii. TraPPE
       iii. AUA4
       iv. TAMie

2. Propane

   (a) Saturation
       i. Potoff
       ii. TraPPE
       iii. AUA4
       iv. TAMie
   (b) T293 highP
       i. Potoff

      ii. TraPPE

     iii. AUA4

     iv. TAMie

3. n-Butane

  (a) Saturation

      i. Potoff

     ii. TraPPE

    iii. AUA4

     iv. TAMie

  (b) T293 highP

      i. Potoff

     ii. TraPPE

    iii. AUA4

     iv. TAMie

Repeat for all other compounds with corresponding potentials

7.3 Finite-size effects

1. Simulation results for 100, 200, 400, and 800 molecules

7.4 Simulation length effects

1. Verified that 1 ns is long enough for larger compounds

7.5 Validation Runs

1. Ethane NIST

2. n-Octane Literature

7.6 Bond types, Harmonic vs LINCS

1. Propane and n-butane with harmonic (arbirary bond constant) shows systematic increase

7.7 Green-Kubo analysis

1. Raw data, i.e., multiple replicates with the average

2. Exclude low time data and have a heurestic for determining the cut-off time

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

7.8 MCMC?