

Responses to Reviewer Comments for: FPE-D-18-00637

Improvements and limitations of Mie λ -6 potential for prediction of saturated and compressed liquid viscosity

by

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Overview

We are grateful for the comments and feedback we received from each reviewer. Specifically, we are encouraged that the reviewers found the manuscript well-written, of high importance, and in need of only minor revisions. We believe that the review process has strengthened this manuscript and that it is now ready to be published. We appreciate your consideration of the revised manuscript for publication in *Special Issue of Fluid Phase Equilibria on Molecular Simulation*.

Itemized List of Changes to Manuscript (Page numbers refer to revised manuscript.)

Response to Reviewer 1, Comment 1: p 12
Response to Reviewer 1, Comment 2: None
Response to Reviewer 1, Comment 3: p 13
Response to Reviewer 1, Comment 4: pp 5, 8
Response to Reviewer 1, Comment 5: p 10
Response to Reviewer 1, Comment 6: pp 5, 6, 21
Response to Reviewer 2, Comment 1: p 3
Response to Reviewer 2, Comment 2: p 4
Response to Reviewer 2, Comment 3: p 5
Response to Reviewer 2, Comment 4: p 27 and SI.VIII. of Supporting information
Response to Reviewer 2, Comment 5: p 30
Response to Reviewer 3, Comment 1: None
Response to Reviewer 3, Comment 2: p 30

Reviewer #1

General

The manuscript reports the results of a significant body of work and is very well-written. I consider it to be publishable in Fluid Phase Equilibria, after consideration of the following optional points is made by the authors. To summarize I think this is a useful addition to the field suitable for publication in the journal, Fluid Phase Equilibria.

Comment #1

The GK formula for the viscosity given in Eq. (1) involves the shear stress $\tau_{\alpha\beta}$. Was this calculated from the atomistic or molecular stress tensor models? The molecular definition is easier to implement as, at least formally, the implicit bond constraint forces would need to be considered in the atomistic stress definition. Although the consequences of this I would suggest are likely to be relatively minor for the present molecules.

Response #1

We utilize the atomic stress tensor as this is the only option in GROMACS. The GROMACS code does, however, account for the implicit bond constraint forces. To clarify this point, we have included the word "atomic" when defining the stress tensor on page 12.

Comment #2

The GK method applied to the shear viscosity is notorious in regard to its statistical inefficiency and many papers have been written on its convergence behavior. The running integral of the time correlation function is quite reasonably fitted to a double exponential form (see eq. (8) in the manuscript). In the paper by R. Hartkamp, P.J. Daivis and B.D. Todd, Phys. Rev. E 87, 032155 (2013), they used the same but with the addition of a gaussian term which represents better the short time part of the correlation function, i.e., the 'ballistic' region. (In fact, strictly speaking all time correlations should be even expansions in time.) In practical terms this might not affect the shear viscosity value too much, but would be worth considering in future studies, especially as the correlation function is largest as $t \rightarrow 0$.

Response #2

We appreciate the reviewer providing the reference to Hartkamp et al. as it could be worth considering in future work. Indeed, the addition of a gaussian term allows for more accurate representation of the short time part of the correlation function. Fortunately, the approach we utilize does not need to fit the short time part because we exclude all data before $t = 3$ ps (per recommendation of Zhang et al.) and we fit the running integral rather than the time correlation function itself. For these reasons, no changes were made to the present manuscript.

Comment #3

It would be useful to add a figure or two showing some representative time correlation functions and their running integrals, together with their fits.

Response #3

We agree with the reviewer and have provided a representative correlation function, Green-Kubo integral, and fits in the Supporting Information. We direct the reader to the supporting information on page 13.

We provide an example of an autocorrelation function, Green-Kubo integral, and this analysis process in Section SI.VI. of Supporting Information.

Comment #4

It appears that all the potential models use in the simulations were of the UA or AUA (anisotropic united atom) construction forms. It would have been interesting to have seen these viscosity predictions compared with those from corresponding fully-atomistic (i.e., including explicit hydrogens) potential models (if they exist), at least for a few test cases. In regard to the force fields actually used, it would be informative to have some indication in broad terms of what the principal differences between them are.

Response #4

Although simulating fully-atomistic force fields would be very interesting, we feel that this is outside of the scope of the manuscript. Several other studies have compared atomistic and united-atom models, which we cite in the introduction. The purpose of this study is to show the improvements that have been achieved by the more modern united-atom models. To make it clear why we are not testing AA models, we have modified the following sentence on page 5:

Furthermore, considering the significant increase in computational cost of AA simulations, two promising alternatives have been investigated to improve the less-expensive UA and AUA force fields

We agree that it is important to discuss the differences between the force fields. We believe that, for the most part, the present manuscript already provides such a comparison. For example, page 5 explains how each is a variation of the united-atom Mie λ -6 potential. The first paragraph of Section 2.1 on page 6 discusses how some are UA and some are AUA force fields.

The one important omission is that we do not discuss the different values of λ . Although we report the different values of λ in Table 4, we do not emphasize this in the main text. For this reason, we have included the following statement on page 8:

Notice that Potoff and TAMie utilize Mie 16-6 and Mie 14-6 potentials, respectively, whereas TraPPE, TraPPE-2, and AUA4 are LJ 12-6 based force fields. As the repulsive barrier at close distances is steeper with increasing λ , the Potoff non-bonded potential is the “hardest” while TraPPE, TraPPE-2, and AUA4 have the “softest” non-bonded potentials.

Comment #5

Perhaps one should not be too surprised that the interaction cut-off distance, r_c , has a non-negligible effect on the viscosity, as the effective potential used is then, $\phi(r) - \phi(r_c)$. Was a tapering function for $r > r_c$ used, for at least some of the cases? This would reduce the sensitivity of the viscosity results to the choice of cut-off. Item [27] in the bibliography is not fully clear.

Response #5

In most cases the cut-off distance does not affect the viscosity (see Section 4.3). We do not use a tapering function as this is not the prescribed method for the given force fields. We have made two changes on page 10 to clarify what type of tail corrections are used in this study.

First, we now direct the reader to Section 4.9 of the GROMACS manual. The discussion therein is clear and too detailed for the present manuscript, but by including the specific section it should be obvious what type of cut-offs we employ. Second, we moved a simplified and modified version of Item 27 to the main text on page 10:

Analytical non-bonded tail corrections for internal energy and pressure are applied in all cases (see Section 4.9 of Reference [29]). Note that GROMACS neglects the long-range contribution from the repulsive (r^{-12}) term as it is several orders of magnitude smaller than the attractive (r^{-6}) contribution. With this simplification, the energy and pressure corrections are proportional to $\epsilon\sigma^6r_c^{-3}$.

Comment #6

Perhaps some more discussion on the relative merits of UA and fully atomistic modelling could be added in the Introduction. In this regard, the paper [J. P. Ewen, C. Gattinoni, F. M. Thakkar, N. Morgan, H. Spikes and D. Dini, Materials, 2016, 9, 651] may be useful.

Response #6

We appreciate the reviewer providing this reference. We have incorporated Ewen et al. into our discussion regarding united-atom vs all-atom models. The following additions are made on pages 5, 6, and 21:

- Included reference for Ewen et al. [24] when listing studies that have investigated AA vs UA
- “Despite AA force fields being more physically realistic, most do not provide quantitatively reliable viscosities and some are actually less accurate than their simpler UA counterparts”
- (we are aware of only three reported viscosity values with the Potoff force field for normal or branched alkanes [24])
- Surprisingly, Ewen et al. report that the Potoff (UA Mie 16-6) force field significantly under predicts viscosity for *n*-hexadecane at a pressure of 202.7 MPa and a temperature of 423 K

Reviewer #2

General

This article contains a systematic evaluation of the capabilities of some usual force fields to provide shear viscosity of some linear and branched alkanes over a wide range of pressures. This article is very well written and clear. The work has been done using an up to date methodology in a very careful way. The results are sensible and will be useful for the transport property community. I have nevertheless minor comments to be addressed before publication

Comment #1

Page 3: It would have been meaningful to cite some references on viscosity experimental data under high pressures published in the literature (Assael and co-workers, Abramson and co-workers, Boned and co-workers ...).

Response #1

We agree with the reviewer and are grateful for the references. Page 3 now includes citations for five experimental measurement articles, including one from each of the groups mentioned by the reviewer.

Comment #2

Page 4: It is stated that entropy scaling approach requires a reference viscosity and an adequate equation of state. This statement is not fully valid, as excess entropy can be deduced from molecular

simulations (e.g. Goel et al., J. Chem. Phys. 129, 2008) and some entropy scaling approach does not require a reference viscosity (e.g. Galliero et al., J. Chem. Phys. 134, 2011)

Response #2

We appreciate the thoroughness of the reviewer. It is true that molecular simulation is capable of providing excess entropy without the need for an equation of state. It is also true that there are several different types of entropy scaling approaches (as shown by Bell [11]). However, even Galliero et al. utilizes a “reducing” viscosity for each method they consider. Therefore, we believe that part of the confusion is our use of the term “reference viscosity.” To clarify this point, we have modified the sentence on page 4 by adding the words “typically” and “or ‘reducing’ viscosity”. We also include a follow-up sentence expressing the role molecular simulation can play.

While entropy scaling has a stronger theoretical basis, it **typically** requires a non-arbitrary choice of the reference **or “reducing”** viscosity [Reference to Galliero et al. and additional source] and an adequate equation-of-state, which may not be readily available for the compound of interest. Note that combining entropy scaling with molecular simulation can help alleviate both of these limitations [References to Goel et al. and Galliero et al. as well as two other additional sources].

Comment #3

-Page 5: It would be interesting to discuss as well what is known on the advantages (and limits) of Mie type potential when used to deal with transport properties of quasi spherical molecules (e.g. Galliero et al., J. Chem. Phys. 129, 2008; Bohling et al., J. Chem. Phys. 140, 2014 ...).

Response #3

We agree with the reviewer. We have included the following statement on page 5 to inform the reader that the Mie potential is not as useful for quasi spherical molecules:

While the LJ 12-6 potential ($\lambda = 12$) is near optimal for predicting viscosities of small, pseudo-spherical molecules [References to three studies of Galliero et al.], the Mie λ -6 potential (with $\lambda \neq 12$) provides considerable improvement for united-atom models of larger, non-spherical molecules.

Comment #4

Page 25: Why choosing a dimensionless distance to compare the RDF? It would have been useful to show the real units results as well.

Response #4

The dimensionless distance was chosen to help determine why Potoff over estimates viscosity at high densities and pressures but the other force fields do not. A plot in real units is not as helpful for this purpose because each force field has a different value of r_{\min} . However, as a plot in real units is more common and could be useful for other reasons, we now include such a plot in Section SI.VIII. of supporting information. We also include a reference to the SI on page 27 of main text:

RDFs with respect to non-reduced distance (r) are found in Section SI.VII. of Supporting Information.

Comment #5

Page 29: The discussion on possible numerical artefacts (finite size, cut off ...) is really interesting. There exist recent works that tackles that problem in details which could be of interest to the authors (e.g. Leonard et al., J. Chem. Theory Comput. 14, 2018).

Response #5

We are grateful for the reviewer bringing the article of Leonard et al. to our attention. We mention the primary conclusion of this study in the opening sentence for Section 4.3 "Cut-off distance" on page 30:

Viscosity, like many other properties, is highly sensitive to the treatment of long-range tail corrections [Reference Leonard et al.].

In addition, we found another recent article by Kim et al. that discusses the role of finite size effects on viscosity. We have modified our discussion in the final paragraph of Section 4.2 "Finite-size effects" on page 30 to reflect the results from their study:

The small fluctuations in $\eta_{\text{liq}}^{\text{sat}}$ with respect to $N^{-\frac{1}{3}}$ for dense systems are consistent with the recent findings of Kim et al. Due to these oscillations, extrapolating to...

Reviewer #3

This is a comprehensive and carefully executed work comparing the performance of various force fields on predicting alkane viscosities. The authors show that a Mie-type potential with exponent > 12 yields superior performance, even against anisotropic models. The authors carefully describe how they do their simulations, do an excellent job of data analysis and uncertainty estimation and write in a clear style. It is a very nice paper and I have only two comments.

Comment #1

The authors say they look at 4 force fields but lump TraPPE and TraPPE-2 together. They are really different force fields so maybe there are 5 studied?

Response #1

Defining what constitutes a "different force field" can be somewhat arbitrary when the force field only has parameters for ethane and ethylene. For example, TAMie also reports CH₃ specific parameters for ethane, but that does not seem to merit any distinction. In this case, we prefer grouping the TraPPE and TraPPE-2 force fields together so that we do not appear to be inflating the number of force fields we test.

Comment #2

The authors make all the force fields have the same intramolecular terms and the same cutoff (with some small exceptions). However, I think the original force fields did not have all these similarities. Those intramolecular terms and details like cutoff are part of the "force field" and so I think it would be correct to say that the original force fields are slightly modified. The authors should clearly discuss this and I think need to state that they are most interested in probing the nonbonded parameters. Please explain why you made all the intramolecular parameters the same.

Response #2

The intramolecular potential used by the original authors of the TraPPE, Potoff, and TAMie force fields are the same as those used in this study. Only the torsional intramolecular terms for AUA4 are different, but we don't simulate any molecules that have torsions with AUA4. For this reason, no change is made regarding the intramolecular terms.

The cutoff prescribed by TraPPE and TAMie is 1.4 nm and for Potoff it is 1.0 nm, which are the same as reported by the corresponding authors. The cut-off for AUA4 in the original publication was 1.0 nm, but the developers of AUA4 subsequently used cut-off values of 1.2 nm and “half the box length”, which is typically greater than 1.4 nm. For this reason, the use of a 1.4 nm cutoff with AUA4 seems justified. To clarify this issue, we have modified the discussion on page 30:

The results presented previously implement a 1.4 nm cut-off for TraPPE, TraPPE-2, and TAMie but a 1.0 nm cut-off for Potoff, as these are the cut-off lengths implemented by the respective authors. Note that the AUA4 developers utilize cut-off distances of 1.0 nm, 1.2 nm, and equal to half the box length (which is typically larger than 1.4 nm for the systems studied). For simplicity, our AUA4 results are obtained using a 1.4 nm cut-off.