# **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 6

Response to Reviewer 1, Comment 2: p 4

Response to Reviewer 1, Comment 3: Numerous minor changes

Response to Reviewer 1, Comment 4: p 4

Response to Reviewer 1, Comment 5: Numerous minor changes

Response to Reviewer 1, Comment 6: p 4

Response to Reviewer 2, Comment 1: p 6

Response to Reviewer 2, Comment 2: p 4

Response to Reviewer 2, Comment 3: Numerous minor changes

Response to Reviewer 2, Comment 4: Numerous minor changes

Response to Reviewer 2, Comment 5: Numerous minor changes

Response to Reviewer 3, Comment 1: p 4

Response to Reviewer 3, Comment 2: p 4

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 . 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 BLANK.

**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 .

***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

**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.

**Comment #5**

Perhaps one should not be too surprised that the interaction cut-off distance, rc, has a

non-negligible effect on the viscosity, as the effective potential used is then, . Was

a tapering function for r > rc 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 to clarify this point. First, we 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 are employed. Second, we moved a simplified and modified version of Item 27 to the main text on page BLANK:

Analytical non-bonded tail corrections for internal energy and pressure are applied in all cases (see Section 4.9 of Reference \cite{GROMACS\_2018}). Note that GROMACS neglects the long-range contribution from the repulsive () term as it is several orders of magnitude smaller than the attractive contribution. With this simplification, the energy and pressure corrections are proportional to .

**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 by making the following additions:

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. We have included citations for BLANK on page BLANK.

**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

**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

**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 so that we could determine why Potoff was overly repulsive at high densities and pressures. A plot in real units is not as helpful for comparing Potoff with TraPPE and TAMie. We now include a plot in real units in 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”:

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 Section 4.2 “Finite-size effects” to reflect the results from their study:

The small fluctuations in with respect to 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. For example, TAMie also reports CH3 specific parameters for ethane. In this case, we prefer grouping the TraPPE and TraPPE-2 force fields into a single class because TraPPE-2 is only available for ethane.

**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 BLANK:

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.