# **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 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

**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 it 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 have

**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***

We

**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, \_(r) − \_(rc). 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***

We strongly

**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 have added to the discussion of united-atom vs. all-atom models. We have also included the reference of Ewen et al.

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 have addressed this issue in Response #5 to the editor. See page 6 of manuscript.

**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) -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 #2***

We agree with the reviewer and have moved “common pitfalls” to the second major bullet point in both checklists (see page 4).

**Comment #3**

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 #3***

After

**Comment #4**

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 #4***

After

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***

This is

**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***

This is