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**Fluid Phase Equilibria,**

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**Improvements and limitations of Mie  $\lambda - 6$  potential**

**for prediction of saturated and compressed liquid viscosity.**

This manuscript reports the results of an extensive equilibrium Molecular Dynamics investigation of the effects of united atom intermolecular potentials on the shear viscosity using the popular Green-Kubo, GK, method. United atom models for molecules are usually significantly more computationally less expensive than their fully atomistic counterparts. The authors use improved united atom potentials of the more general Mie  $\lambda - 6$  form for the excluded volume interactions rather than just the Lennard-Jones (LJ) 12:6 special case which shows improved viscosity values compared with LJ. The values of  $\lambda$  are typically larger than 12, which seems reasonable as the fully atomistic model with explicit hydrogens will be stiffer than the previous united atom potentials based on the LJ potential. The shear viscosity is a particularly demanding test of a force field. A wide range of short and long organic molecules was considered. It was shown that the interaction cut-off distance can have a significant effect on the computed viscosity. Some non-negligible system size effects were also observed in certain cases. Agreement of the computed viscosities with the REFPROP ‘database’ is generally quite good, *inter alia* validating the simulation method.

The report gives much technical detail and assessments of statistical accuracy.

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.

## **Points**

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.

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  $t \rightarrow 0$ .

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.

4. It appears that all the potential models used 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.

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.

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.

To summarize I think this is a useful addition to the field suitable for publication in the journal,

Fluid Phase Equilibria.