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Comment on amt-2022-151

Markus Petters (Referee)

Referee comment on "A new hot-stage microscopy technique for measuring temperature-dependent viscosities of aerosol particles and its application to farnesene secondary organic aerosol" by Kristian J. Kiland et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2022-151-RC2>, 2022

Kiland et al. show how a microscope interfaced with a hotplate can be used to measure the temperature dependence of viscosity for samples where less than 1 mg of material is available. The technique is compared against one substance with known temperature dependence of viscosity. It is further shown that the technique can be applied to secondary organic material collected from an environmental chamber experiment. These data are discussed in the context of parameterization-to-data comparison.

The presented technique is a new addition to the toolbox of scientists who are interested in measuring the viscosity of organic aerosols. The underlying techniques are sound. I am excited to see this work being pursued and I recommend the paper for publication. However I have some suggestions on how the data interpretation might be improved.

Comments:

The technique focuses on bulk samples. Therefore secondary organic material should be used throughout to distinguish it from aerosol sampling.

TaNB was heated above the melting point of $\sim 185^\circ\text{C}$ and then cooled to generate glassy material. This step is not mentioned for the SOM. Presumably, the particles turned glassy in the chamber or the -20°C freezer. Was heating of the SOM avoided due to the possibility of evaporation of more volatile components, thermal decomposition, and thermally induced chemical reactions? Furthermore, not all crystalline substances can be heated above the melting point without decomposition. Presumably this is the reason why sucrose - a seemingly more logical choice to validate the system due to its widespread use in the community - was not used. It would be helpful to add some discussion that highlights the assumptions and limitations associated with the sample preparation

requirements.

The abstract and manuscript puts a lot of emphasis on the comparison with the DeRieux et al. parameterization, showing that the observed values were “significantly higher (1–2 orders of magnitude)” than values predicted by a parameterization. I have some concerns regarding this framing. Foremost, the emphasis in the abstract distracts from the fact that this is a methods paper that has the main purpose to show that viscosity can be measured for small samples, as shown by the comparison with the TaNB bulk data. The SOM experiment nicely demonstrates that the measurement on collected samples from smog chambers is feasible. The apparent discrepancy to a parameterization is probably neither significant nor particularly important in the context of the known experimental and modeling uncertainties.

The model in this manuscript heavily relies on the assumption of $D = 10$ from DeRieux et al. and zero error in the T_g prediction. The pure component data underlying the $D = 10$ estimate has significant scatter. We actually report $D = 7$ for α -pinene SOA (Petters and Kasparoglu, 2020), which is an almost direct measurement. The overestimated viscosity by 1-2 orders of magnitude reported in the abstract is based on the assumed D and trusting that T_g is known perfectly. I do not believe that better closure should be expected given the uncertainty in composition, aerosol measurement, and uncertainties in the parameterization.

Figure 7 explores the temperature dependence of viscosity for the SOA in the context of D , showing that no single D value can reproduce the measurements. As discussed in DeRieux et al. and further explored in Petters and Kasparoglu, T_g current viscosity data for α -pinene SOA imply a scatter in the estimated T_g of $\pm 25\text{K}$ or with constrained D parameter and hygroscopicity $\pm 10\text{K}$ (see their Figure 3 and the associated text). Tethering Figure 7 in Kiland to a single T_g value is thus not quite appropriate. Furthermore, T_g can take on a range of values depending on the cooling rate of the substance, or in the case of the chamber the way that the SOA was formed. It would seem more logical to fit the temperature dependent viscosity data using a constant D value and extrapolate the fit to 10^{12} Pa s to find the T_g . The procedure could be repeated for a range of D values that the authors believe might be plausible. This is similar to the procedure we used in Rothfuss and Petters (2017) and Marsh et al. (2018), where we find that extrapolated T_g from a VFT fit compares to $\pm 10\text{K}$ with literature values for select substances. Comparing the extrapolated T_g from the measurements to the predicted T_g likely results in closure within a reasonable interval.

Regardless, given the uncertainty in aerosol chemical composition, the possibility of source fragmentation of farnesene SOA during HRMS measurement, the possibility of sample aging via partial evaporation during storage or due to chemical reactions, and the possibility that the parameterization is simply insufficient to model T_g precisely for all compositions, agreement or disagreement with the DeRieux parameterization is too unconstrained to reach all but the broadest conclusion that the data presented here are reasonable. The subtleties associated with the experiment/parameterization comparison, however, should be more thoroughly discussed in the manuscript.

Other comments

"Rothfuss and Petters used a dimer relaxation technique to measure viscosities of SOA in the range of 5×10^5 to 2×10^7 Pa s at temperatures ranging from -15 to 80 °C (Rothfuss and Petters, 2016)"

Rothfuss and Petters did not apply this technique to SOA. Application to SOA is reported in S.Petters et al. (2019) and Champion et al. (2019)

"On the other hand, this means samples cannot be collected and measured at a different time and different location using this technique."

I do not understand the value of location and time in this context. The fundamental limitation of the dimer relaxation technique as described in Rothfuss and Petters is the availability of sufficient number concentration, which makes it difficult to apply the technique to aged aerosol in environmental chambers. However, absent this limitation, it would be preferable to not have to separate the particles from the gas-phase and measure it "then and there".

"The area and L were determined from the sequence of binary images using a MATLAB script."

The programming language is probably not important here. However, it would be helpful to state the type of image analysis that was applied as well as the potential limitations. For example, does the analysis use edge detection? Is it sensitive to lighting conditions? Does the analysis require adjustment of parameters to get it right or does it work fully automated out of the box?

References Cited

Champion, W. M.; Rothfuss, N. E.; Petters, M. D.; Grieshop, A. P. Volatility and Viscosity Are Correlated in Terpene Secondary Organic Aerosol Formed in a Flow Reactor. *Environ. Sci. Technol. Lett.* 2019, 6 (9), 513–519. <https://doi.org/10.1021/acs.estlett.9b00412>.

Marsh, A.; Petters, S. S.; Rothfuss, N. E.; Rovelli, G.; Song, Y. C.; Reid, J. P.; Petters, M. D. Amorphous Phase State Diagrams and Viscosity of Ternary Aqueous Organic/Organic and Inorganic/Organic Mixtures. *Phys Chem Chem Phys* 2018, 20 (22), 15086–15097. <https://doi.org/10.1039/C8CP00760H>.

Petters, S.; Kreidenweis, S. M.; Grieshop, A. P.; Ziemann, P. J.; Petters, M. D. Temperature- and Humidity-Dependent Phase States of Secondary Organic Aerosols. *Geophys. Res. Lett.* 2019, 46 (2), 1005–1013. <https://doi.org/10.1029/2018GL080563>

Petters, M. D.; Kasparoglu, S. Predicting the Influence of Particle Size on the Glass Transition Temperature and Viscosity of Secondary Organic Material. *Sci. Rep.* 2020, 10 (1), 15170. <https://doi.org/10.1038/s41598-020-71490-0>.

Rothfuss, N. E.; Petters, M. D. Characterization of the Temperature and Humidity-Dependent Phase Diagram of Amorphous Nanoscale Organic Aerosols. *Phys Chem Chem Phys* 2017, 19 (9), 6532–6545. <https://doi.org/10.1039/C6CP08593H>.