DeRieux et al. present an extension of their recent model that predicts the viscosity of organic aerosol particles as a function of their simplified chemical composition, using elemental ratios. They have extended the model, largely using data recently compiled by Rothfuss and Petters (2017), to include organics with a molar weight up to $\sim 1100$ g/mol, from the original 450 g/mol. The motivation for this work is to predict the diffusivity of organic aerosol, as this /may/ have important limitations for vapor uptake and growth, water uptake and CCN activation, equilibration timescales, etc. It is important to note that this model only estimates the glass transition temperature, from which viscosity can in turn be estimated, and from this an estimate of diffusivity can be made. So, there are many critical steps along to way to deriving the actual property of interest,
and the uncertainties involved in each of these steps needs to be discussed fully in this manuscript.

Following the careful clarification and further discussion of several important aspects in this manuscript it should be acceptable for publication in ACP. The topic is within scope though personally I think there has been an over-abundance of effort spent recently on viscous organic aerosols. The significance and novelty of the research presented here is quite low by ACP standards, as it merely extends a recent model, and the model's predictions involve an important series of significant assumptions and estimations, and yet the actual diffusivity is still not arrived at. If I was interested in predicting viscosity or diffusivity I personally would turn to Rothfuss and Petters’ functional group-based method. It provides deeper chemical insight, since viscosity and diffusivity are created by the interactions between molecules and their functional groups/dipoles. Still, if the major issues with this method and manuscript are satisfactorily addressed, there is nothing technically wrong with this paper to prevent its publication. I do think the authors could be addressing this topic in a deeper and more comprehensive way, and I hope my comments can be used to improve the paper. Referee #2 also raised several excellent points that also need to be fully addressed.

Introduction (page 3-4): The potential importance of viscous organic aerosol phases is really over stated here. As many other papers have done, most of the important implications of viscous organics are predicted but few have actually been demonstrated through laboratory or ambient experiments using real complex atmospheric aerosol or reasonable proxies. The authors are cherry picking the results to motivate their work. For example, the slow evaporation of SOA referred to is observed after a significant fraction of the SOA promptly evaporated. The slowly evaporating SOA remaining cannot be distinguished from the effects of diffusional limitations or just being too darn low in volatility. The viscosity of alpha-pinene SOA was recently studied in a more direct manner using optical tweezers and no significant limitations to diffusion were reported (Gorkowski et al., 2017). The authors are also ignoring highly relevant novel experi-
ments from Neil Donahue’s group where they use aerosol population experiments to evaluate the very condensation growth limitations that these authors posit are an important consequence of viscous SOA. Yet Ye et al. did not observe impediments to mixing expect at quite low RH (Ye et al., 2016). Scot Martin’s group has approached this topic from a different perspective (Liu et al., 2016). And I see Ye et al. has extended these experiments to study toluene and some other systems as well: Ye, Q., Upshur, M. A., Robinson, E. S., Geiger, F. M., Sullivan, R. C., Thomson, R. J. and Donahue, N. M.: Following Particle-Particle Mixing in Atmospheric Secondary Organic Aerosols by Using Isotopically Labeled Terpenes, Chem, doi:10.1016/j.chempr.2017.12.008, 2018.


Page 3: Particle bounce measurements are not a reliable assessment of viscosity, and certainly not of diffusivity. These measurements may have started the focus on viscous phases but the measurement methods have advanced considerably since then. What we really need are measurements of the diffusivity of different types of molecules in atmospheric aerosols.

Line 57: Truly direct measurements of viscosity are difficult to achieve with the small mass loadings of aerosol available. Were these truly "direct" measurements of viscosity? More likely they were inferred from poke-flow or bead transport measurements.
Like 63: It is odd that the important plasticization effects of water vapor uptake are not mentioned anywhere near this section on retarded water vapor uptake. Water uptake will reduce viscosity and these transport limitations.

Line 72: Effects of slow water uptake on ice nucleation properties is one of those effects that has been proposed but I do not think there is direct evidence for this. Certainly not in realistic complex aerosol particles.

Line 84: The highly related study by Rothfuss and Petters really warrants much further discussion here. Their paper significantly advanced the methods we can use to understand and predict viscosity and diffusivity, and did this from a function group perspective. This manuscript also borrows heavily from the extensive dataset compiled by Rothfuss and Petters, and that paper deserves more credit for enabling the modeling presented in this manuscript under consideration. Later in this paper there also needs to be a solid comparison of this model to the functional group based one of Rothfuss and Petters.

Page 86: This is an inaccurate statement; we are getting more and more molecular-level understanding of organic aerosols and their vapor precursors, such as from CIMS, and also FT-IR, Raman, and other analysis methods. While molecular-based analysis is more challenging than just reducing the measurements to simple elemental ratios, molecules can still be measured, they are what matter, and this is not a valid justification for relying on HCO ratios. You could refer to the large existing datasets from the AMS for example that only reduce the organic aerosol to its elemental ratios as a motivation for an atomic ratio-based model.

Section 2: I have a series of concerns regarding how viscosity is measured here. The uncertainties in the various parameters and estimates involved need to be properly discussed, and these uncertainties propagated to provide an uncertainty range for the actual estimate of viscosity. The parameterization begins with an estimate of the melting point, Tm, from the EPA EPI Suite. Then the glass transition point, Tg, is estimated
from Tm. How accurate are these estimates, especially for the types of molecules relevant for atmospheric aerosol? Was the EPA model trained on these sorts of models? Or you not use Tm in this new model since Eqn. (2) does not depend on Tm? In the end you state that Eqn. (1) can only be used for M < 450 g/mol but Eqn (2) is not suitable for use in common models such as the VBS. Since Eqn (1) will still be used these important aspects regarding the uncertainties in Tm and Tg need to be clarified.

Line 183: Please explain the free volume theory and topological constraint theory.

Page 213: "Water mass fraction can be estimated using the effective hygroscopicity parameter". This likely will not capture the small but important mass fraction of water uptake at low RH that leads to significant plasticization and reduction of viscosity. You need to discuss if there is experimental evidence supporting the use of growth factor derived water uptake measurements to describe the effects of water on Tg and viscosity.

Line 218: Another estimate, dependence of viscosity on temperature, requiring an estimate of the fragility constant, D. Sensitivity calcs are provided in Section 3 for the value of D, but no discussion of the accuracy of Eqns. 4 & 5 are presented.

Giving the fragility parameter the symbol "D" is an unfortunate choice since diffusivity is usually represented by D as well, and isn't the diffusivity of molecules in aerosol particles the parameter that really matters, not the viscosity?

Line 255: Please explain and justify the free volume assumption.

Line 256: Please briefly discuss this more "profound meaning" of the Vogel temperature. There are a lot of concepts and terms used here that are not familiar to the atmospheric chemistry audience.

Line 267: There are highly relevant measurements of viscosity of SOA, or of its impacts (or lack thereof) on mixing timescales that are missing here, such as the papers by Ye, Gorkowski, and Liu mentioned above.
Line 269: Up to what RH values is the viscosity of alpha-pinene SOA significant? My understanding of the literature is that above a rather low RH threshold of 20-30%. I think the importance of viscosity is again being overstated here, and again the mixing experiments are a better direct probe of how viscosity might affect vapor uptake and growth. This needs to be discussed more quantitatively than referring to "low RH".

Line 281: "The wide range of viscosities reported for $\alpha$-pinene SOA may indicate that the O:C values may be different in different experiments." This frankly is quite sloppy. The average O:C value will change just with changes in aerosol mass concentration, as the less volatile components are typically more oxidized. And then there are all the important effects of using different chemical aging mechanisms to form the SOA. Not to mention the interesting effects of water vapor itself on the chemical composition of SOA. How is this accounted for? The plasticization effect of increased water vapor is important but it also changes the reaction products, as these authors recently reported: Hinks, M. L., Montoya-Aguilera, J., Ellison, L., Lin, P., Laskin, A., Laskin, J., Shiraiwa, M., Dabdub, D., and Nizkorodov, S. A.: Effect of relative humidity on the composition of secondary organic aerosol from the oxidation of toluene, Atmos. Chem. Phys., 18, 1643-1652, https://doi.org/10.5194/acp-18-1643-2018, 2018.

Line 305: The high sensitivity of predicted viscosity to Tg is really concerning considering that Tg is estimated from Tm, which is also estimated from the EPA EPI Suite model. The effect of varying D and kappa is briefly discussed, but what is critically missing is an assessment of the accuracy and uncertainty in the predicted viscosity. When you consider how many steps are taken to calculate viscosity, and how sensitive it is to Tg, I am left with little confidence in this model’s predictions.

Line 325: See comment above for Line 281. The important roles of aerosol mass loading and other experimental conditions can be discussed in a much more meaningful and quantitative manner. We have a pretty good grasp of how the aerosol mass loading affects partitioning, volatility, O:C, and thus predicted viscosity, yet here it is presented as some nebulous unconstrained factor.
Sect. 3.2: Refer to the recent mixing experiments involving toluene by Ye et al.

Line 381: Analyte solubility in the solvent used is also an important factor in the detection efficiency using DESI.

Line 386: The key role of aerosol loadings is again treated very vaguely. What were the mass loadings for these two different experiments? The OFR method typically works at much much higher loadings than in a large smog chamber. Please be specific here. There is no need to treat the aerosol loading as some unknown factor.

Sect. 3.3: The analysis of biomass burning particles, while valiant, is really unsatisfying. First, why weren’t experiments on BBA when AMS data is available to provide elemental analysis used? Surely there must be experiments on BBA where AMS and the other necessary measurements were made? If not I suggest this entire section be omitted, as the results are terrible, because the input data from the experiments does not properly constrain the model. The exclusion of CHOS and CHON compounds from the model is a problem for BBA, where organonitrates are common components, and organosulfates can be as well. It seems that applying the model to BBA is too premature. The authors could move this to the SI if they think there is some value in the exercise.

Line 460: "Current Tg parameterizations do not consider functionality or molecular structure explicitly and further measurements of Tg and viscosity of SOA would allow us to refine the method presented in this study." This is precisely why the functional group-based approach of Rothfuss and Petters is vastly superior than the Tg based approach here, and yet this closely related alternate model is barely discussed here.

As mentioned earlier, in the end you get an estimate of viscosity (following a series of steps with their own uncertainties), but the property that really matters is diffusivity, and unfortunately the Stokes-Einstein relationship between viscosity and diffusivity is inaccurate by more than one order of magnitude in high viscosity systems (Marshall et al., 2016). So it is not clear to me what this rather simplistic estimate of viscosity from
Tg really tells us about important aerosol physicochemical properties in the end.

As Referee 2 pointed out, there is little data > 500 g/mol plotted in Fig 3a to fit to.

Fig. 4a: The slope of the experimental data is quite different from the predicted lines. Please discuss as this is concerning. The experimental data has a much shallower slope. A similar discrepancy is seen in Fig. 5. These issues give me even less confidence in the model.

Fig. 10 would be much more meaningful if the estimated mixing/equilibration timescale was added to the right y-axis. Just plotting it as viscosity is not meaningful to most readers. The important effect is how viscosity affect diffusivity, which determines equilibration timescales. You will need to discuss the important issues of converting between viscosity and diffusivity.

References


