Response to the comments of Anonymous Referee #1
(Referee comments in black, our responses in blue)

Referee general comment 1:

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 ~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.

Thank you for your comments. While we acknowledge the importance of the diffusion coefficient, the primary purpose of this paper is to predict the glass transition temperature and viscosity for SOA mixtures using a bottom up approach (as specified in title, abstract and throughout the text) that can be used to make predictions of viscosity from soft-ionization high-resolution mass spectrometry data and be incorporated into atmospheric models. We are fully aware that estimations of bulk diffusivity involve multiple steps and that the Stokes-Einstein equation can be used for conversion of viscosity to bulk diffusivity for first-order approximation, but this relation may break down in highly viscous systems (Power et al., Chem. Sci., 2013; Marshall et al., Chem. Sci., 2016; Chenyakin et al., 2017). Bulk diffusion of small molecules such as water and ozone should be treated separately, for example using obstruction theory or percolation theory (e.g., Shiraiwa et al., PNAS, 2011; Bones et al., PNAS, 2012; Berkemeier et al., ACP, 2014; Price et al., ACP, 2015). In this study, we focus on estimations of T_g and viscosity. Estimations of bulk diffusivity in the SOA material are beyond the scope of this study.

We agree that the functional group model by Sastri and Rao (1992), as used by Rothfuss and Petters (2017), is a valuable method to predict the viscosity of a single pure organic compound when the chemical structure is known. Rothfuss and Petters (2017) demonstrated the influence of functional groups on viscosity of pure organic compounds, but did not provide a method to predict viscosity of complex multi-component SOA mixtures. In addition, the chemical structures of SOA components are often not known, whereas their elemental formulae can be determined in HR-MS measurements, and our method is able to provide practical estimates of T_g, making use of these measurements. Also, there are not yet any regional or global air quality models that explicitly treat functionality of SOA compounds. On the other side, the viscosity estimation method presented in our work is applicable in a global model (e.g., Shiraiwa et al., 2017) and the T_g prediction method developed in this study can be practically applied for example in the SOM model (Cappa and Wilson, 2012; Jathar et al., 2015). Thus, we are confident that this study is valuable and it would merit publication in ACP.

Comment 2: 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 experiments 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. The authors need to present the motivation behind studying viscous aerosol phases in a more precise and balanced manner, distinguishing between those effects that have been speculated, and those for which there is actual significant experimental evidence (especially from realistic atmospheric aerosol). Here for example is an interesting documented effect of phase state causing differential growth of aerosol particles: Zaveri, R. A., Shilling, J. E., Zelenyuk, A., Liu, J., Bell, D. M., D'Ambro, E. L., Gaston, C. J., Thornton, J. A., Laskin, A., Lin, P., Wilson, J., Easter, R. C., Wang, J., Bertram, A. K., Martin, S. T., Seinfeld, J. H. and Worsnop, D. R.: Growth Kinetics and Size Distribution Dynamics of Viscous Secondary Organic Aerosol, Environ. Sci. Technol., 52(3), 1191-1199, doi:10.1021/acs.est.7b04623, 2018.

Following the reviewer's suggestion, we have extended the introduction to discuss previously missed relevant studies as indicated below:

Lines 56-59: "SOA particles were observed to evaporate unexpectedly slowly (Cappa and Wilson, 2011; Vaden et al., 2011), and recent modeling studies have evaluated the contributions of low diffusivity and volatility to slow evaporation rates (Roldin et al., 2014; Yli-Juuti et al., 2017)."
Lines 79-88: "Partitioning of semi-volatile compounds into viscous particles may result in kinetically-limited growth in contrast to quasi-equilibrium growth (Perraud et al., 2012; Shiraiwa and Seinfeld, 2012; Booth et al., 2014; Zaveri et al., 2014; Mai et al., 2015; Liu et al., 2016), which also affects the evolution of particle size distribution upon SOA growth (Shiraiwa et al., 2013; Zaveri et al., 2018). Chamber experiments probing mixing timescales of SOA particles derived by oxidation of various precursors such as isoprene, terpene, and toluene have observed strong kinetic limitations at low RH, but not at moderate and high RH (Loza et al., 2013; Ye et al., 2016; Ye et al., 2018). Gorkowski et al. (2017) did not observe significant diffusion limitations for glycerol and squalene in α-pinene SOA. Quasi-equilibrium versus kinetically-limited or non-equilibrium SOA growth remains an open issue and warrants further investigations. "

Comment 3: 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.

Even though bounce experiments do not provide robust viscosity measurements, they can give useful insights into the particle phase state and provide rough estimates of viscosity (Bateman et al., 2014; Bateman et al., 2015). As such, the results from these studies are represented with shaded boxes in our figures to represent the estimated viscosity. Additionally, we strongly agree that direct measurements of bulk diffusivity are needed (Chenyakin et al., 2017).

Comment 4: Line 59: 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.

In the references cited at Line 59, viscosities were inferred from measurements, such as poke-flow measurements, beam mobility measurements, and fluorescence lifetime imaging measurements. To address the referee's comment, "direct" will be removed from Line 59.

Comment 5: Line 70: 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.

We are fully aware of the plasticizing effect of water and we consider hygroscopic growth and use the Gordon-Taylor approach to account for this effect. We have clarified this point in the revised manuscript by adding the following text:

Lines 50-51: "The phase state is also strongly affected by relative humidity, as water can act as a plasticizer to lower viscosity (Mikhailov et al., 2009)."

Lines 226-228: "SOA particles contain a number of organic compounds as well as a variable amount of liquid water, which has low T_g (136 K) and can act as a plasticizer (Mikhailov et al., 2009; Koop et al., 2011)."

Comment 6: Line 73: 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.

Direct experimental evidence for the effect of slow water uptake on ice nucleation properties has been reported by multiple groups for model organic compounds (Murray et al., 2010; Schill et al., 2014), laboratory generated SOA (Wang et al., 2012a; Ignatius et al., 2016; Charnawskas et al., 2017), and ambient SOA particles (Wang et al., 2012b). A comprehensive review on this topic was published very recently (Knopf et al., 2018). We have added additional references in the revised manuscript.

Comment 7: Line 89: 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.

We agree that the functional group model by Sastri and Rao, as used by Rothfuss and Petters, is a valuable method to predict the viscosity of single pure organic compound when the functional groups and structure of that compound are known. However, such an approach does not include a method for determining T_g or viscosity of multi-component mixtures (Rothfuss and Petters, 2017). To direct readers to their valuable work, we have added the following statement to our manuscript.

Lines 89-91:"Group contribution methods have been used to predict the viscosities of pure compounds when the functionality and molecular structure are known (Sastri and Rao, 1992; Rothfuss and Petters, 2017)."

Lines 98-99:"These studies provide important insights in estimating the viscosity of individual organic compounds."

Comment 8: Line 98: 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.

We have deleted this sentence in the revised manuscript.

Comment 9: 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.

Please note that both Eq. (1) and (2) are developed based on experimental T_g data. Eq. (1) is developed based on 178 CH and CHO compounds with measured T_g compiled by Koop et al. (2011) plus 3-methylbutane-1,2,3-tricarboxylic acid (3-MBTCA), an atmospheric oxidation product of α-pinene with its measured T_g of 305 ± 2 K (Dette et al., 2014). Eq. (2) is developed based on the above 179 compounds plus the experimental T_g data compiled in Rothfuss and Petters (2017).

As measurements of T_g for atmospheric SOA components are scarce (Dette et al., 2014), as shown in Fig. 1c in the manuscript, we validate our parameterization by comparing the T_g predicted by Eq. (2) (referred as "predicted T_g") with both measured T_g (Koop, et al., 2011; Dette et al., 2014; Rothfuss and Petters 2017) as well as estimated T_g for 654 SOA components following the Boyer-Kauzmann rule with their melting temperature T_m (referred as "estimated T_g" in our manuscript), which has been validated by Koop et al. (2011). Thus, the Boyer-Kauzmann rule is used with an attempt to validate the ability of Eq. (2) applied in atmospheric organic components. The new figure Fig. A2(a) shows that the Boyer-Kauzmann rule works well to estimate T_g. For the 654 SOA components (Shiraiwa et al., 2014), as shown in Fig. 1c in the manuscript, even though T_m from the EPI Suite is adopted (because the measured T_m are not always available), Eq. (2) can constrain those compounds reasonably well. Regarding the uncertainty in T_g predictions, as we wrote in the manuscript, T_g of individual compounds can be predicted within ±21 K as indicated by the prediction band (dotted lines in Fig. 1c).

In short summary, both Eq. (1) and (2) are developed based on experimental T_g and the Boyer-Kauzmann rule estimating T_g by T_m is only used for comparison with Eq. (2) predictions. We agree with the reviewer's note that Eq. (1) can be applied in the VBS more easily. As we wrote in the manuscript, regarding the application in aerosol models, Eq. (2) may be suitable for coupling with the statistical oxidation model which characterizes the SOA evolution as a function of n_C and n_O (Cappa and Wilson, 2012; Jathar et al., 2015). Eq. (2) is more flexible than Eq. (1) to bring in the compounds containing hetero-atoms (e.g., nitrogen or sulfur) in future studies.

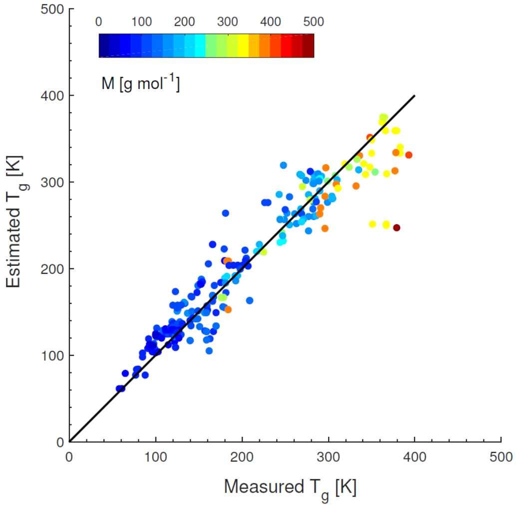


Figure A2(a). Comparison of measured and estimated T_g by the Boyer-Kauzmann rule for 251 organic compounds (Koop et al., 2011; Dette et al., 2014; Rothfuss and Petters 2017) with their measured T_m available. The markers are color-coded by molar mass.

Comment 10: Line 200: Please explain the free volume theory and topological constraint theory. Line 288: Please explain and justify the free volume assumption.

We have further explained these concepts by revising our manuscript as follows:

Lines 200-207: "The correlation between T_g and the number of carbon atoms is consistent with the free volume theory, in which molecular motion is restricted by the difference between the space required for a molecule to vibrate versus the space in which the molecule resides (i.e. the free volume) (White and Lipson, 2016). The correlation between T_g and the number of OH groups is more consistent with the topological constraint theory where the primary influence is the three dimensional structure of the molecule as determined by such factors as molecular bonds and hydrogen-bonding networks (Nakanishi and Nozaki, 2011; van der Sman, 2013).

Comment 11: Page 240: "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.

We have added the following discussion in the revised manuscript as follows:

Lines 245-249: "Pajunoja et al. (2015) found that water uptake in subsaturated conditions is inhibited until RH is high enough for dissolution of water in SOA particles with relatively low O:C ratios. As oxidation of SOA increases, solubility of water *increases and dissolution occurs at lower RH values. In both cases, the use of subsaturated hygroscopicity measurements was supported."*

Lines 227-229: "SOA particles contain a number of organic compounds as well as a variable amount of liquid water, which has low T_g (136 K) and can act as a plasticizer (Mikhailov et al., 2009; Koop et al., 2011). Under humid conditions, SOA particles take up water by hygroscopic growth in response to RH, lowering T_g and viscosity of SOA particles."

Comment 12: Line 259: 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?

These equations are well established in the glass community as detailed in cited references (Angell, 1995, 1997). The symbol for fragility strength, D, is used by the glass community and we have chosen to maintain this convention. In our previous publications, we used 'D_b' for bulk diffusivity. Please note that diffusivity estimations are beyond the scope of this study (see our response to the first comment).

Comment 13: Line 288: 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.

We have revised the manuscript to clarify this concept as follows:

Line 288-295: "For the WLF equation, T_g is the reference temperature and there is a linear dependence assumed between temperature and free volume (O'Connell and McKenna, 1999; Huang and McKenna, 2001; Metatla and Soldera, 2007). For the VTF equation, the reference is the Vogel temperature (T_0)–a hypothetical temperature at which all non-vibrational motion ceases and viscosity becomes infinite and the theoretical foundation of the VTF equation includes both thermodynamic and kinetic considerations (O'Connell and McKenna, 1999; Huang and McKenna, 2001; Metatla and Soldera, 2007)."

Comment 14-16: Line 305: 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 317: 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". Sect. 3.2: Refer to the recent mixing experiments involving toluene by Ye et al. 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.

The goal of this section is to compare our viscosity estimation method with viscosity measurements—estimations of bulk diffusivity and mixing timescales are beyond the scope of this study. We also do not discuss the effects of viscosity on vapor uptake and particle growth. Equilibration timescale is not only a function of viscosity and bulk diffusivity, but it also depends strongly on other factors including accommodation coefficient, particle number concentration, and particle size (Shiraiwa and Seinfeld, 2012). Thus, even though we agree that equilibration timescales would be highly important, they are beyond the scope of this study. The suggested references are included in the introduction (see our response 1).

Comment 17: Line 307: "The wide range of viscosities reported for α-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.

Even though the O:C ratio can affect the phase state, the O:C ratio of SOA were unfortunately unavailable for most studies, with the exception of Zhang et al (2015) which reported O:C =~0.46. We agree that RH upon SOA formation can affect chemical composition and phase of SOA particles (Kidd et al., 2014; Hinks et al., 2018). We have revised the manuscript to clarify this point as follows:
Lines 307-314: "The wide range of experimentally measured viscosities reported for α-pinene SOA, particularly from 30-60% RH is most likely a consequence of the different experimental approaches, mass loadings and O:C ratios for each experiment. For instance, Grayson et al. (2016) used mass loadings of 121 to 14000 μg m^{-3} *and observed that viscosity decreased as mass loading increased. Higher mass loadings would lead to greater partitioning of semi-volatile and lower molar mass compounds into the particle phase, which would lead to the decrease of* T_g *and viscosity of the resulting SOA mixture. They concluded that their results should be considered a lower limit for viscosity of α-pinene SOA in the atmosphere."*

Comment 18: Line 351: 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.

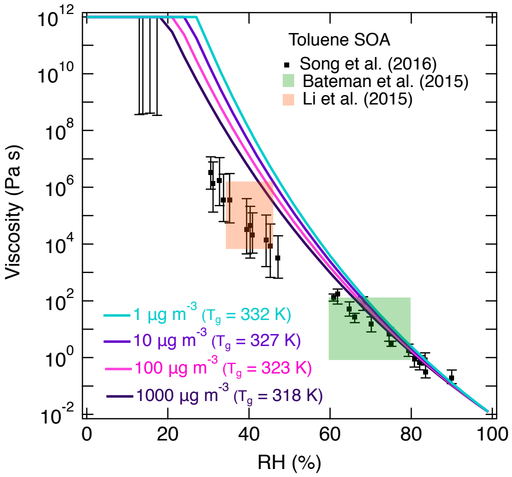
Please refer to response 9. Our T_g parameterization is developed from experimental T_g and the Boyer-Kauzmann rule using T_m is used only for comparison. Note that the T_g of isoprene and α-pinene SOA used in Figs 4-6 are adopted from Table A1 in Berkemeier et al. (2014) who showed the T_g of isoprene and α-pinene SOA varied with O:C. We did not use Eq. (1) or (2) to predict the T_g of isoprene and α-pinene SOA here because elemental composition of SOA for different experiments was unavailable. Thus, the performance of viscosity predictions of isoprene and α-pinene SOA shown in Figs 4-6 has no relation to Eq. (1) or (2). For viscosity predictions, VTF and WLF equations are established and validated in the glass community. In fact, these equations have also been widely used in the atmospheric community to predict the viscosity of SOA mixtures (Berkemeier et al., 2014; Wang et al., 2015; Schill et al., 2013; Maclean et al., 2017; Rothfuss and Petters, 2017a, 2017b; Pratap et al., 2018). Figure 4 in our manuscript shows that the VTF predictions assuming D of 10 agree well with the WLF predictions.

Comment 19: Line 329: See comment above for Line 307. 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.

We agree that mass loading can affect viscosity, as it affects the chemical composition of SOA particles. Grayson et al. (2016) observed a decrease in α-pinene SOA viscosity when mass loading increased, with a factor of 45 decrease in viscosity observed when mass loading increased from 121 to 14000 μg m^{-3} at <0.5% RH. Song et al. (2016) investigated this effect for toluene SOA produced at two different mass loadings (60-100 and 600-1000 μg m^{-3}) and compared their results to previous studies on toluene SOA by Bateman et al. (2015) (30-50 μg m^{-3}) and Li et al. (2015) (44-125 μg m^{-3}). They did not observe a significant effect of mass loading on viscosity, concluding that toluene SOA mixtures are not very sensitive to mass loading effects.

To follow up on this issue, we carried out a sensitivity study of mass loadings on viscosity of toluene SOA using HR-MS data. The saturation mass concentration (C^0) was predicted for each component using the molecular corridor approach (Li et al., 2016). Assuming that the mass signal intensity is proportional to the total mass of the compound in the mixture, and applying the absorptive partitioning theory (Pankow, 1994), particle-phase concentrations of each compounds were estimated at different mass loading values (1-1000 μg m^{-3}) followed by T_g and viscosity estimations for each mass loading using the scaled particle-phase concentrations. Mass loading effects on viscosity can be clearly observed in new Fig. A3: as mass loading increases, the glass transition temperature of the SOA mixture and the viscosity decrease. At low RH, the predicted viscosities span up to two orders of magnitude, while at high RH they have little difference. The mass loading effect is smaller than that observed when model parameters ($T_{g,org}$, κ, k_{GT} and D) are varied and its overall effect is not large, which is consistent with Song et al. (2016). Mass loading effects may warrant further investigations with dedicated experiments combined with modeling partitioning and viscosity predictions. We have added the following text to our manuscript:

Lines 1015-1021:



"Figure A3. *Effect of mass loading on predicted viscosity for toluene SOA. Solid lines represent the predicted viscosity with Eq.(2) using chemical composition of toluene SOA formed at low RH. Viscosity was predicted with different mass loadings ranging from 1-1000 µg m^{-3}. Markers and shaded boxes represent experimentally measured viscosity values. Song et al. (2016) mass loadings were 60-100 and 600-1000 µg m^{-}3. Bateman et al., (2015) and Li et al., (2015) mass loadings were 30-50 µg m^{-3} and 44-125 µg m^{-3}, respectively."*

Lines 307-314: "The wide range of experimentally measured viscosities reported for α-pinene SOA, particularly from 30-60% RH is most likely a consequence of the different experimental approaches, mass loadings and O:C ratios for each experiment. For instance, Grayson et al. (2016) used mass loadings of 121 to 14000 µg m^{-3} and observed that viscosity decreased as mass loading increased. Higher mass loadings would lead to greater partitioning of semi-volatile and lower molar mass compounds into the particle phase, which would lead to the decrease of T_g and viscosity of the resulting SOA mixture. They concluded that their results should be considered a lower limit for viscosity of α-pinene SOA in the atmosphere."

Lines 447-460: "In addition, different mass loadings may have affected viscosity. Song et al. (2016) measured viscosity at two different mass loadings (60-100 and 600-1000 µg m^{-3}) and compared their results to Bateman et al. (2015) (30-50 µg m^{-3}) and Li et al. (2015) (44-125 µg m^{-3}), observing little impact of mass loadings on viscosity. We carried out a sensitivity study of mass loadings on viscosity using a set of compounds detected by HRMS. The saturation mass concentration was predicted for each component using the molecular corridor approach (Li et al., 2016). Assuming that the mass signal intensity is proportional to the total mass concentration of the compound in the mixture, and applying the absorptive partitioning theory (Pankow, 1994), particle-phase concentrations of each compound were predicted to estimate T_g at different organic aerosol mass loading values (1-1000 µg m^{-3}). The glass transition temperature of the

SOA mixture decreases as mass loading increases. Viscosity decreases up to two orders of magnitude at low RH, while at high RH they have little difference as shown in Fig. A3. Simultaneous measurements of viscosity and chemical composition with different mass loadings should be performed in future studies."

Comment 20: Line 390: Analyte solubility in the solvent used is also an important factor in the detection efficiency using DESI.

We agree that the choice of solvent is an important factor for this characterization method. We selected the solvent to maximize solubility and ionization efficiency of OA compounds in ESI. For SOA, acetonitrile or methanol represent a good choice because they extract all of the organics from the sample and provide stable ESI conditions (Hinks et al., 2017).

Comment 21: Line 387: 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.

The mass loadings for the experiment are listed at the beginning of the section. We have also added them to the caption for Figure 7 in the revised manuscript:

Lines 974-975, Figure 7 caption: "Mass loadings were 23 μg m^{-3} *for LRH and 8 μg* m^{-3} *for HRH (Hinks et al., 2017)."*

Comment 22: 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.

The point of our analysis is to compare the predicted viscosity with HRMS data using two different ionization methods. Our intention was not to provide accurate estimates of viscosity of BBA especially since, as the referee also pointed out, we do not currently have equations to predict T_g for N and S containing compounds. The value of Section 3.3 is enabling a comparison of data from the ESI and APPI methods to discuss the variability in the modeling prediction. For this reason, we opted to include this section in the main manuscript. To clarify this point we added the following text:

Lines 478-480: "Please note that we do not intend to provide accurate estimates of ambient biomass burning particles (as inorganic components are also not included in this analysis), but we investigate how the use of different ionization methods would lead to *variations in our viscosity predictions."*

Comment 23: Line 531: "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 T_g really tells us about important aerosol physicochemical properties in the end.

As we mentioned in the above responses, Rothfuss and Petters (2017) did not provide a method to predict viscosity of complex multi-component SOA mixtures. Diffusivity estimations are beyond the scope of this study and will be investigated in future studies (please see response 1).

Comment 24: As Referee 2 pointed out, there is little data > 500 g/mol plotted in Fig 3a to fit to.

Please see our response to Referee 2.

Comment 25: 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.

As illustrated in Figures 5(d) and 6(d), the slope of the curve decreases at low RH if the values of k_{GT} or κ are lower at 1.0 or 0.05, respectively. However, the curve does not fit well at high RH with this value of k_{GT}. Available experiments indicate that k_{GT} should be around 2-3 (Dette et al., 2014; Dette and Koop, 2015). We acknowledge that our method has certain limits, which need to be investigated further.

References:

Angell, C. A.: Formation of glasses from liquids and biopolymers, Science, 267, 1924-1935, 1995.

Angell, C. A.: Entropy and fragility in supercooling liquids, National Institute of Standards and Technology, Journal of Research, 102, 171-185, 1997.

Bateman, A. P., Belassein, H., and Martin, S. T.: Impactor Apparatus for the Study of Particle Rebound: Relative Humidity and Capillary Forces, Aerosol Sci. Technol., 48, 42-52, 2014.

Bateman, A. P., Bertram, A. K., and Martin, S. T.: Hygroscopic Influence on the Semisolid-to-Liquid Transition of Secondary Organic Materials, J. Phys. Chem. A, 119, 4386-4395, 2015.

Booth, A. M., Murphy, B., Riipinen, I., Percival, C. J., and Topping, D. O.: Connecting Bulk Viscosity Measurements to Kinetic Limitations on Attaining Equilibrium for a Model Aerosol Composition, Environ. Sci. Technol., 48, 9298-9305, 2014.

Cappa, C. D., and Wilson, K. R.: Evolution of organic aerosol mass spectra upon heating: implications for OA phase and partitioning behavior, Atmos. Chem. Phys., 11, 1895-1911, 2011.

Cappa, C. D., and Wilson, K. R.: Multi-generation gas-phase oxidation, equilibrium partitioning, and the formation and evolution of secondary organic aerosol, Atmos. Chem. Phys., 12, 9505-9528, 2012.

Charnawskas, J. C., Alpert, P. A., Lambe, A., et al.: Condensed-phase biogenic-anthropogenic interactions with implications for cold cloud formation, Faraday Discuss., 200, 165-194, 2017.

Chenyakin, Y., Ullmann, D. A., Evoy, E., Renbaum-Wolff, L., Kamal, S., and Bertram, A. K.: Diffusion coefficients of organic molecules in sucrose–water solutions and comparison with Stokes–Einstein predictions, Atmos. Chem. Phys., 17, 2423-2435, 2017.

Dette, H. P., Qi, M., Schröder, D. C., Godt, A., and Koop, T.: Glass-forming properties of 3-Methylbutane-1,2,3-tricarboxylic acid and its mixtures with water and pinonic acid, J. Phys. Chem. A, 118, 7024-7033, 2014.

Dette, H. P., and Koop, T.: Glass Formation Processes in Mixed Inorganic/Organic Aerosol Particles, J. Phys. Chem. A, 119, 4552-4561, 2015.

Gorkowski, K., Donahue, N. M., and Sullivan, R. C.: Emulsified and Liquid–Liquid Phase-Separated States of α-Pinene Secondary Organic Aerosol Determined Using Aerosol Optical Tweezers, Environ. Sci. Technol., 51, 12154-12163, 2017.

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, 2018.

Ignatius, K., Kristensen, T. B., Järvinen, E., et al.: Heterogeneous ice nucleation of viscous secondary organic aerosol produced from ozonolysis of α-pinene, Atmos. Chem. Phys., 16, 6495-6509, 2016.

Jathar, S. H., Cappa, C. D., Wexler, A. S., Seinfeld, J. H., and Kleeman, M. J.: Multi-generational oxidation model to simulate secondary organic aerosol in a 3-D air quality model, Geosci. Model Dev., 8, 2553-2567, 2015.

Kidd, C., Perraud, V., Wingen, L. M., and Finlayson-Pitts, B. J.: Integrating phase and composition of secondary organic aerosol from the ozonolysis of alpha-pinene, Proc. Natl. Acad. Sci. U.S.A., 111, 7552-7557, 2014.

Knopf, D. A., Alpert, P. A., and Wang, B.: The Role of Organic Aerosol in Atmospheric Ice Nucleation: A Review, ACS Earth and Space Chemistry, 2018.

Koop, T., Bookhold, J., Shiraiwa, M., and Pöschl, U.: Glass transition and phase state of organic compounds: dependency on molecular properties and implications for secondary organic aerosols in the atmosphere, Phys. Chem. Chem. Phys., 13, 19238-19255, 2011.

Li, Y., Pöschl, U., and Shiraiwa, M.: Molecular corridors and parameterizations of volatility in the chemical evolution of organic aerosols, Atmos. Chem. Phys., 16, 3327-3344, 2016.

Liu, P., Li, Y. J., Wang, Y., Gilles, M. K., Zaveri, R. A., Bertram, A. K., and Martin, S. T.: Lability of secondary organic particulate matter, Proc. Natl. Acad. Sci. U.S.A., 113, 12643-12648, 2016.

Loza, C. L., Coggon, M. M., Nguyen, T. B., Zuend, A., Flagan, R. C., and Seinfeld, J. H.: On the mixing and evaporation of secondary organic aerosol components, Environ. Sci. Technol., 47, 6173-6180, 2013.

Mai, H., Shiraiwa, M., Flagan, R. C., and Seinfeld, J. H.: Under What Conditions Can Equilibrium Gas–Particle Partitioning Be Expected to Hold in the Atmosphere?, Environ. Sci. Technol., 49, 11485-11491, 2015.

Mikhailov, E., Vlasenko, S., Martin, S. T., Koop, T., and Pöschl, U.: Amorphous and crystalline aerosol particles interacting with water vapor: conceptual framework and experimental evidence for restructuring, phase transitions and kinetic limitations, Atmos. Chem. Phys., 9, 9491-9522, 2009.

Murray, B. J., Wilson, T. W., Dobbie, S., et al.: Heterogeneous nucleation of ice particles on glassy aerosols under cirrus conditions, Nat. Geosci., 3, 233-237, 2010.

Nakanishi, M., and Nozaki, R.: Systematic study of the glass transition in polyhydric alcohols, Physical Review E, 83, 051503, 2011.

Pankow, J. F.: An absorption model of gas-particle partitioning of organic-compounds in the atmosphere, Atmos. Environ., 28, 185-188, 1994.

Perraud, V., Bruns, E. A., Ezell, M. J., et al.: Nonequilibrium atmospheric secondary organic aerosol formation and growth, Proc. Natl. Acad. Sci. U.S.A., 109, 2836-2841, 2012.

Roldin, P., Eriksson, A. C., Nordin, E. Z., et al.: Modelling non-equilibrium secondary organic aerosol formation and evaporation with the aerosol dynamics, gas- and particle-phase chemistry kinetic multilayer model ADCHAM, Atmos. Chem. Phys., 14, 7953-7993, 2014.

Rothfuss, N. E., and Petters, M. D.: Influence of Functional Groups on the Viscosity of Organic Aerosol, Environ. Sci. Technol., 51, 271-279, 2017.

Sastri, S. R. S., and Rao, K. K.: A new group contribution method for predicting viscosity of organic liquids, The Chemical Engineering Journal, 50, 9-25, 1992.

Schill, G. P., De Haan, D. O., and Tolbert, M. A.: Heterogeneous Ice Nucleation on Simulated Secondary Organic Aerosol, Environ. Sci. Technol., 48, 1675-1682, 2014.

Shiraiwa, M., and Seinfeld, J. H.: Equilibration timescale of atmospheric secondary organic aerosol partitioning, Geophys. Res. Lett., 39, L24801, 2012.

Shiraiwa, M., Yee, L. D., Schilling, K. A., Loza, C. L., Craven, J. S., Zuend, A., Ziemann, P. J., and Seinfeld, J. H.: Size distribution dynamics reveal particle-phase chemistry in organic aerosol formation, Proc. Natl. Acad. Sci. U.S.A., 110, 11746-11750, 2013.

Vaden, T. D., Imre, D., Beranek, J., Shrivastava, M., and Zelenyuk, A.: Evaporation kinetics and phase of laboratory and ambient secondary organic aerosol, Proc. Natl. Acad. Sci. U.S.A., 108, 2190-2195, 2011.

van der Sman, R. G. M.: Predictions of Glass Transition Temperature for Hydrogen Bonding Biomaterials, J. Phys. Chem. B, 117, 16303-16313, 2013.

Wang, B. B., Lambe, A. T., Massoli, P., Onasch, T. B., Davidovits, P., Worsnop, D. R., and Knopf, D. A.: The deposition ice nucleation and immersion freezing potential of amorphous secondary organic aerosol: Pathways for ice and mixed-phase cloud formation, J. Geophys. Res.-Atmos., 117, D16209, 2012a.

Wang, B. B., Laskin, A., Roedel, T., Gilles, M. K., Moffet, R. C., Tivanski, A. V., and Knopf, D. A.: Heterogeneous ice nucleation and water uptake by field-collected atmospheric particles below 273 K, J. Geophys. Res.-Atmos., 117, D00v19, 2012b.

White, R. P., and Lipson, J. E. G.: Polymer Free Volume and Its Connection to the Glass Transition, Macromolecules (Washington, DC, U. S.), 49, 3987-4007, 2016.

Ye, Q., Robinson, E. S., Ding, X., Ye, P., Sullivan, R. C., and Donahue, N. M.: Mixing of secondary organic aerosols versus relative humidity, Proc. Natl. Acad. Sci. U.S.A., 113, 12649-12654, 2016.

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, 4, 318-333, 2018.

Yli-Juuti, T., Pajunoja, A., Tikkanen, O.-P., et al.: Factors controlling the evaporation of secondary organic aerosol from α-pinene ozonolysis, Geophys. Res. Lett., 44, 2562-2570, 2017.

Zaveri, R. A., Easter, R. C., Shilling, J. E., and Seinfeld, J. H.: Modeling kinetic partitioning of secondary organic aerosol and size distribution dynamics: representing effects of volatility, phase state, and particle-phase reaction, Atmos. Chem. Phys., 14, 5153-5181, 2014.

Zaveri, R. A., Shilling, J. E., Zelenyuk, A., et al.: Growth Kinetics and Size Distribution Dynamics of Viscous Secondary Organic Aerosol, Environ. Sci. Technol., 52, 1191-1199, 2018.