Response to Referee comments (comments in black, response in blue)

Anonymous Referee #1

Summary + General Comments

In "Estimation of Secondary Organic Aerosol Viscosity from Explicit Modeling of Gas-Phase Oxidation of Isoprene and α -pinene," Galeazzo et al. present the use of GECKO-A modeling on isoprene and α -pinene SOA to model the chemical composition and calculate the viscosity at various relative humidities. Though experimental samples, either from real-world conditions or from controlled conditions in a chamber, can lead to measurements of viscosity, global climate models will not be accurate solely using viscosity data from a small number of locations or test chambers. Numerous factors, including environmental (e.g. T, RH), chemical (e.g. compound structure, functional group contribution, atomic ratios), and physical (e.g. partitioning) processes, can contribute to large variance in aerosol behavior, e.g. glass transition temperature and viscosity. Recent progress made in parameterizing the prediction of viscosity has reduced the necessary inputs to elemental composition, stopping short of functional group analysis, thus providing a different pathway for viscosity prediction through high-resolution mass spectrometry.

Experimentally, viscosity of aerosol has been determined using a few different methods/instruments, e.g. poke flow mobility, a differential mobility analyzer, a particle impactor coupled with scanning electron microscopy, or a rebound impactor. By taking the priors from those experiments (precursor concentration, ozone concentration, T, RH, reaction time) and running those through GECKO-A, the researchers were able to predict glass transition temperatures and viscosities, which they could then compare to the experimental values.

When comparing modeled to experimental isoprene SOA viscosity with respect to relative humidity, the modeled values were found to be within error to experimental values assuming a hygroscopicity of 0.10. The modeled viscosity values for α -pinene were underestimated by 1 to 4 orders of magnitude, though wide experimental uncertainties led to some experimental values possibly lining up with the model. Better agreement was found between modeled and experimental values when mass loading was varied. A few interesting breakdowns of chemical composition were displayed as well.

Finally, the authors tried varying the mass accommodation coefficient, a property that measures how likely a gas molecule approaching an aerosol will be taken up. They selected two starting experimental conditions from a couple of different papers and observed a stark contrast between the expected viscosity vs. RH curves when predicting using a mass accommodation coefficient from unity to an effective value dependent on penetration depth.

This article is generally well-written, has a logical flow and is well-organized, has a clear description of results, and presents clear and concise graphs. The authors properly point out where future research remains and do well in pointing out subtleties in the models and the data. The section on varying the mass accommodation coefficient is novel, considering the same lab recently published the work on effective mass accommodation coefficients (Shiraiwa and Pöschl, 2020). Some sentences have interesting phrasing, which I will point out in the subsequent "technical corrections" section. I would tentatively recommend this article for publication, provided the authors address the following points.

We thank Referee #1 for the review and positive evaluation of our manuscript.

My biggest concern is a notable similarity of the first few figures in this paper and their corresponding results/discussion paragraphs to the paper Gervasi et al. published in early 2020, also in ACP (Gervasi et al., 2020). Comparing Figures 1 and 2 in Galeazzo et al. (this paper) to Figure 7a and 7c in Gervasi et al., we can note that Gervasi et al. incorporate data from more studies in their figure, specifically from the Bateman et al. study for the isoprene SOA and the Abramson et al. and Pajunoja et al. studies for the α -pinene SOA. Perhaps for the pinene experiments, this is because each of these papers only have one data point each and they use different experimental techniques than the ones mentioned here? These two papers remain different because the Gervasi et al. study uses MCM instead of GECKO-A with box modeling; however, this paper by Galeazzo et al. is missing any reference to Gervasi et al. Additionally, Galeazzo et al.'s paper, by means of chronology, would benefit from a comparison of the effectiveness of their model to the one found in Gervasi et al. While their isoprene SOA models yield fairly similar results in the viscosity vs. RH space, the α -pinene SOA data in Gervasi et al. appear to outperform the Galeazzo et al. model, bringing into question whether this paper represents an improvement on previously published methods. In theory, GECKO-A's model is more detailed and provides many more minor reactions pathways that the MCM does not. However, it is unclear whether this extra information makes the model more accurate or if these results point to some shortcoming in GECKO-A's processing.

We would like to note that the viscosity prediction method in Gervasi et al. (2020) relies on the T_g parametrization and viscosity prediction method that we have developed in our group (DeRieux et al., 2018): Figure 7a and 7c of Gervasi et al. (2020) are based upon and similar to Figure 4a and 4b in DeRieux et al. (2018), respectively. While Figure 4a of DeRieux et al. included Abramson and Bateman studies, we could not simulate Abramson's and Pajunoja's experiments in this study because unfortunately there is insufficient information to reproduce their experimental conditions as several experimental conditions were missing such as reaction time, concentration, temperature, and RH.

Gervasi et al. (2020) analyzed viscosity of α -pinene, isoprene and toluene surrogate mixtures using the AIOMFAC-VISC model. They focused on the impacts of intermolecular effects on the viscosity of organic-water mixtures. The explored solutions were composed by different combinations of water and organic compounds generated during α -pinene and isoprene oxidation in MCM. For predicting the viscosity of SOA, they selected 14-21 representative compounds from the MCM simulations of α -pinene and isoprene oxidation. In order to achieve a better agreement with experimental viscosity measurements, Gervasi et al. (2020) adjusted the composition of the representative α -pinene SOA mixtures to match the O:C ratio found in experimental measurements (Renbaum-Wolff et al., 2013; Grayson et al., 2016). As a result, the model developed by Gervasi et al. (2020) uses surrogate mixtures that cannot explore the effects of different experimental conditions on α -pinene SOA composition and resulting viscosity. Their approximation is valid for the purpose of estimating viscosity once the chemical composition of the particle phase is known, while it cannot explicitly link viscosity measurements with SOA composition generated by specific experimental conditions. Our study distinguishes from Gervasi et al. by providing information on the origins of the variations observed among viscosity measurements by taking into account different experimental conditions of SOA formation in various studies. We highlight how the composition from different experimental setups can impact the final SOA viscosity.

We have clarified this issue and added corresponding discussions in the revised manuscript.

Introduction: "Gervasi et al. (2020) simulated viscosity of aqueous SOA surrogate mixtures derived from oxidation of α -pinene, isoprene and toluene using the AIOMFAC-VISC model combined with the T_g parametrization of DeRieux et al (2018), demonstrating the capability and flexibility of the group-contribution method in predicting the viscosity for organic mixtures of varying degrees of complexity.

There is a strong need for the development of a modelling tool for further elucidation of the impacts of various aerosol properties and processes on particle viscosity. A better understanding of the interplay among gas-phase reactions, chemical composition and viscosity of SOA is essential for further development of model representation of the evolution of SOA in the atmosphere."

One other concern I have with this paper is the current lack of supplementary information. The experimental inputs and/or the model outputs would be useful information to provide for other scientists who wish to investigate such work. Having this more simple data be publicly available, either in the SI or in a repository, would be preferred. The data in Figures 4 and 5 would be helpful in table format for other scientists, while Figure 3 itself may be more efficiently placed in the SI, if it existed.

Following your comment, we compiled the data and model outputs that are used for figures in CSV files and share them in the supplement.

Gervasi et al. paper also builds up validation of the model using various solutions, including pure water, pure single component solutions, and then SOA. This manuscript would benefit from such an analysis, though this is not absolutely necessary for publication.

The purpose of this study is to estimate viscosity of multicomponent mixtures, as generated by GECKO-A. The validation of pure component viscosity and the mixing rule has been explored and validated in a series of our previous studies (Shiraiwa et al., 2017; DeRieux et al., 2018; Li et al., 2020) as well as in Gervasi et al. (2020). We clarify this point in the revised manuscript by adding the below sentence in Sect. 2.3:

"For validation and applicability of T_g parameterizations and the viscosity prediction method, they have been applied to high resolution mass spectrometry data of toluene SOA and biomass burning aerosols (DeRieux et al., 2018), SOA generated by diesel fuels (Song et al., 2019), β -Caryophyllene SOA (Maclean et al., 2021), and surrogate VOC mixtures by healthy and stressed plants (Smith et al., 2021), agreeing well with viscosity measurements."

While GECKO-A provides a plethora of chemical detail, it would be good to know if the researchers, either of this paper or elsewhere, are actively working to overcome the shortcomings and inefficiencies of GECKO-A.

Since the first GECKO-A publication (Aumont et al., 2005), the GECKO-A tool is constantly extended to include new processes, as for example the chemistry of cyclic structures in Valorso et al. (2011), the gas/particle partitioning in Camredon et al. (2008), the gas/aqueous phase

partitioning in Mouchel-Vallon et al. (2013), the gas to chamber wall partitioning in La et al. (2016). In the past 5 years the GECKO-A tool has been extended to deal with the structure and chemistry of aromatic organic compounds, all the SAR included in GECKO-A have been updated on the basis of the latest literature (Jenkin et al., 2018a; Jenkin et al., 2018b; Jenkin et al., 2019; Jenkin et al., 2020), and the addition of recently identified chemical pathways, such as autoxidation, is currently under development. Autoxidation is a challenging matter to deal with. Vereecken and Noziere (2020) recently published a SAR to estimate H-shift in peroxy radical reactions. Although it gives estimates for many structures, multifunctional species remain far outside the scope of the SAR. Some thoughts are in progress to define how to extrapolate the SAR to all the species generated by GECKO-A. Another issue with autoxidation is that including such pathways drastically increase the number of species and reactions in the generated mechanisms, leading to unmanageable chemical schemes. Reduction methods are currently under development to overcome this limitation.

We added a paragraph in the manuscript to highlight the research, the progresses and undergoing developments of GECKO-A:

"GECKO-A is frequently updated to include the newly discovered chemical processes in the mechanism generator: recently, the mechanism generator has been extended to treat the chemistry of aromatic organic compounds based on the latest SAR developments (Jenkin et al., 2018a; Jenkin et al., 2018b; Jenkin et al., 2019; Jenkin et al., 2020). Other recent updates include the chemistry of cyclic structures (Valorso et al., 2011), the gas-aqueous phase partitioning (Mouchel-Vallon et al., 2013), and the gas to chamber wall partitioning (La et al., 2016)."

At the end of the introduction, the authors could provide more detail on the overarching objective. The phrase "to expand our understanding on the relationship and interplay among" is vague, and possibly deliberately so. It would be helpful to provide the reader a quick summary clause at the end of the sentence to tie it back into something concrete, such as incorporation into global models.

We revised the end of introduction to be more concrete as below:

"There is a strong need for the development of a modelling tool for further elucidation of the impacts of various aerosol properties and processes on particle viscosity. A better understanding of the interplay among gas-phase reactions, chemical composition and viscosity of SOA is essential for further development of model representation of the evolution of SOA in the atmosphere. ... The objective of this work is to develop a useful tool for analysis and investigation of SOA chemical composition and phase state and to expand our fundamental understanding on such properties."

At line 206, the authors wrote "Simulation results for Renbaum-Wolff's and Grayson's experiments fall within uncertainties of experimental measurements for the 40-60 % RH range." This observation is clearly true from Figure 2, but the uncertainties for those data points are quite large, spanning 3-5 orders of magnitude, and the experimental data trend higher than the model data. Such a detail may be worth including.

We note that experimental measurements are subject to relatively large uncertainties.

"Simulation results for Renbaum-Wolff's and Grayson's experiments fall within the relatively large uncertainties of experimental measurements for the 40-60% RH range."

At line 220, the authors assert that the variance of model simulations and experimental measurements is very similar and give a correlation coefficient, but provide no data to support this claim. An SI would be useful to give the reader the option to verify this information.

We show the correlation plot as below, while we believe the inclusion of R^2 value is sufficient in the main text. A tabulated version of the final viscosity vs RH data will be provided as a separate file in SI.





Finally, at line 283, the viscosity curves seemed to line up fairly well for the Renbaum-Wolff experiments, but not for the Kidd experiment. Do these results have any bearing on either Kidd et al.'s methodology or results or do they point exclusively toward a general need for more research into how the mass accommodation coefficient should behave over time and chemical composition?

Kidd et al. (2014) provided just a single viscosity estimation point for α -pinene. This viscosity value was not directly measured, but it was inferred from the impaction pattern, which is subject of a large uncertainty. As a result, it is challenging to draw a strong conclusion and further experimental and modeling research is necessary to elucidate impacts of chemical composition and mass accommodation on particle viscosity.

Technical Corrections

This manuscript has a number of sentences that would benefit from a read-through or from reading them out loud. I have also omitted changes I assume will be caught by a copy editor.

Lines 3-6: "In this study, we conduct explicit modeling of isoprene photooxidation and α -pinene ozonolysis and subsequent SOA formation using the GECKO-A (Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere) model. Our recently-developed parameterizations to predict glass transition temperature of organic compounds are implemented into a box model with explicit gas-phase chemical mechanisms to simulate viscosity of SOA."

These sentences are a tad bit awkward, and the authors used "explicitly" twice in quick succession. A possible fix, though this sentence can be fixed in plenty of different ways, is provided below.

"In this study, we use GECKO-A (Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere) to conduct explicit chemical modeling of isoprene photooxidation and α -pinene ozonolysis and their subsequent SOA formation. Coupling this level of chemical detail with box modeling and our recently-developed glass transition temperature parameterizations allows us to predict SOA viscosity."

Following your suggestion, we revised the sentences as below:

"In this study, we apply GECKO-A (Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere) to conduct explicit chemical modeling of isoprene photooxidation and α -pinene ozonolysis and their subsequent SOA formation. The detailed gas-phase chemical schemes generated with GECKO-A are implemented into a box model and coupled to our recently-developed glass transition temperature parameterizations, allowing us to predict SOA viscosity."

Lines 24-25: Change "enabling to generate" to either "capable of generating" or "that can generate."

The sentence has been corrected with "that can generate".

Lines 31-34: It may make sense to combine these two sentences together.

Lines 30-43: Depending on preference, the flow of this paragraph may benefit from lining up the order of each variable as they are first listed with the order of the sentences. To clarify, line 32 states "depending on chemical composition, relative humidity (RH), and temperature." You could move the next two sentences, "Notably, water..." and "It has been observed that..." to after the Petters et al. citation to make sure that subsequent sentences detailing work done with varying chemical composition, then temperature and RH are in closer proximity. Alternatively, or simultaneously, you could make the previous change for lines 31-34, which may make this juxtaposition more compact.

Following your suggestion, it is combined into one sentence.

"The particle phase state is impacted by SOA chemical composition, hygroscopicity, and water content, as water can act as a plasticizer lowering SOA viscosity (Mikhailov et al., 2019)."

Line 44: Change "fast" to "quickly."

The word has been changed as suggested.

Line 87: Inconsistent spelling of "autooxidation" with "autoxidation" elsewhere.

It is corrected to "autoxidation".

Table 1: RH in the heading should be RH (%). Put T and RH next to each other. Either convert the Song isoprene study to ppb or convert the pinene experiments to ppm for consistency. Might be more visually striking to have an extra column on the left with vertical text indicating which precursor is used. As it is, the pinene and isoprene distinction blend in with the table. In footnote, SEM should be written out, since it was not mentioned previously in the manuscript. A footnote to explain reaction time would be useful.

We prefer to keep the legend as is for simplicity. The following changes have been implemented in Table 1: 1) SEM is deleted from the footnote; 2) T and RH are moved close to each other; 3) the unit of RH is specified in %.

Study	O ₃ (ppm)	a-pinene (ppm)	RH (%)	T (K)	t (min.)	Exp. setup*	$T_{\rm g,org}({ m K})$	O:C simulated
Renbaum-Wolff et al., 2013	0.30	0.1	0.5	298	30	Continuous flow. PF-BM	275 K	0.49
Zhang et al., 2015	30	0.7	0.5	293	6	Batch exp., DMA	258 K	0.43
Zhang et al., 2015	30	0.7	0.5	293	1.5	Batch exp., DMA	263 K	0.44
Kidd et al., 2014	0.65	0.8	dry,	297	30	Batch exp., PI	266 K	0.44
Grayson et al., 2016	0.07	0.1	0.5	298	80	Continuous flow, PF-BM	284 K	0.55
Bateman et al., 2015	0.1	0.3	0.5	298	174	Continuous flow, R	275 K	0.48
	O ₃ (ppm)	Isoprene (ppm)	RH (%)	T (K)	t (min.)	Exp. setup*	$T_{\rm g,org}({\rm K})$	
Song et al., 2015	10	4	13.0	293.15	1.4	Continuous flow, PF-BM	260	1.0

* Poke Flow Bead Mobility (PF-BM), Differential Mobility Analyzer (DMA), Particle Impactor (PI), Rebound impactor (R).

Line 183: Change "Results" to "Results and discussion"

The suggested change has been made.

Throughout document, line 187: Copy editor's job, likely, but the 60 and % are on different lines.

We will make sure on this issue upon proof reading.

Figure 1: Could you make the markers slightly larger?

The markers have been enlarged.

Line 203: In previous literature, a hygroscopicity κ of 0.1 for pinene has been shown to fit quite well (Petters and Kreidenweis, 2007; Prenni et al., 2007).

We used $\kappa = 0.1$ based on previous measurements and we did not use it because it leads to better fitting of the data; hence, we would like to keep the original sentence.

Figure 2: Could you add the line and dashed line to the small legend?

We prefer to keep the legend as is for simplicity, while explaining them in the figure caption.

Lines 278-279: Change "low volatile" to "low volatility" or "lower volatility." Also, add a comma after "unity."

The suggested changes have been implemented in the revised manuscript.

Lines 299-302: Swap "by a few orders of magnitude" and "lower than experimental measurements."

The suggested changes have been implemented in the revised manuscript.

"Simulated viscosity values for isoprene SOA are in good agreement with measurements, while those for α -pinene SOA were lower than experimental measurements by a few orders of magnitude."

Line 308 paragraph: Would it make more sense to have some of this paragraph be a discussion section?

We would like to keep this paragraph in this section, as all of simulated experiments formed SOA under dry conditions and SOA was exposed to water only upon viscosity measurements. Thus, we think that discussing this aspect in a discussion section might confuse readers and would like to keep it separate in the conclusion section.

References

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