Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-900-RC3, 2020

Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Predicting Secondary Organic Aerosol Phase State and Viscosity and its Effect on Multiphase Chemistry in a Regional Scale Air Quality Model" *by* Ryan Schmedding et al.

Anonymous Referee #2

Received and published: 26 January 2020

The manuscript by Schmedding et al. investigates the influence of a viscous phase state and phase separation of secondary organic aerosols (SOA) on aerosol mass yields in the Community Multi-Scale Air Quality Model (CMAQ) chemical transport model (CTM). The focus is the effect of a glassy phase state of organic coatings on the acid-catalyzed multiphase reactions of IEPOX. The research topic is timely and would mark a step forward in the important task of porting physical chemical effects of SOA into CTMs. The paper thus falls well within the scope of ACP.

My main scientific critique of this paper regards the concept of semi-solid phase separation (SSPS). What this paper does is calculating when a hypothetical pure organic phase would have a viscosity > 100 Pa·s. If that were the case, the authors assume that this semi-solid phase coats the particles in a core-shell morphology, 100 % of the time. Whether core-shell phase-separation occurs in the real atmosphere depends on many factors, such as molecular O:C ratio of the organic phase, which is not a criterion for SSPS in the model. To my knowledge, it is very unlikely that phase separation occurs simply based on semi-solid viscosity. Assuming phase separation to calculate a viscosity that is in turn used to justify the existence of phase separation is circular logic. The effect of this hypothesis is not tested and evaluated enough, e.g. by a thorough comparison of the PhaseSep and the PhaseSep2 scenario. Inorganic components that typically reduce the viscosity of particles are completely ignored in this part of the model and the discussion in the manuscript. Liquid-liquid phase separation (LLPS) is also tracked in the model, but it is not made clear what impact it has on the model results. Overall, the discussion about phase separation is very dominant in the text and figures of the paper. I thus wonder if the authors should simply de-emphasize the discussion of phase separation. What the authors actually investigate is the effects of diffusion limitation on SOA formation, as the title of the manuscript correctly states, and less so the effect of phase separation. The manuscript text and the discussion does not reflect that. Phase separation is in this paper just a means of getting to ignore the effect inorganics have on diffusion rates.

The overall presentation of this paper needs improvement. Many small inaccuracies make the paper hard to read and cumbersome to review. The authors spent many lines of text enumerating number ranges means and medians that could easily be stored in tables, i.e. viscosities, percentages, diffusion coefficients etc., which makes the text hard to read and to extract a scientific message from it. Furthermore, there are too many grammatical and orthographical errors to point out; some are listed in the technical comments below. The paper is sometimes imprecise in language, especially about phase state and glass transition, e.g. the use of "phase" vs. "phase state" or through use of colloquialisms. The introduction is poorly written, especially in lines 111 to 127.

Please check the references section, some DOI links were improperly formatted and are not working. I agree with referee 1 that formatting of figures can be substantially improved. Labelling and resolution of the figures does not have publication quality. Overall, I would appreciate if the authors would take more time and diligence next time before submission to make the manuscript easier digestible. Unless the discussion of model assumptions and results, as well as the presentation of these results is significantly improved, I cannot recommend this paper for publication in ACP.

Major comments

The authors should clarify the very central assumption in their manuscript that all semi-solid particles > 100 Pa s phase separate. What is this assumption based on? A reference is given (Shiraiwa et al. 2017), but I do not see this manuscript making a statement about phase separation dependent on viscosity. All phase-separation percentages given in the text and figures are dominated by this assumption, but how realistic is it and what does it add to our understanding of SOA? The uncertainty of the SSPS assumption strongly diminishes the validity of total fractions of phase-separated particles in the atmosphere that are prominently discussed in this manuscript (l. 659 – 666). Please add sufficient caveats and error estimates in the appropriate places.

The authors show many figures analyzing their model data. However, the manuscript text is widely used to list these numbers, without much interpretation or discussion. Discussion is often superficial and obvious as indicated in the minor comments below. I would suggest condensing the message of this manuscript to fewer, central figures and discuss them thoroughly.

To avoid confusion, please consider the use of Tg,org instead of Torg for the glass transition temperature of the organic phase throughout the manuscript.

In Fig. 2, it would probably be useful if the liquid to glass transition were marked with a distinct change in color. Here, this important transition lies in the middle of the pink/purple color range.

I do not understand the point of Fig. 3 since it is very hard to see what is going on and do not find it illustrative. It seems that water is the constituent with the highest variability; it is thus very unintuitive to plot it on the base of this plot, especially because a high concentration leads to a low overall value. It would hence be more helpful to not stack these three lines, but just report the diurnal cycle of $T_{g,org}$ along with the particle composition in a separate panel. A graphical representation like the one shown in Fig. S1 seems better suited to present the data.

l. 633 – In the discussion of the PhaseSep2 scenario, it would be very helpful to see how PhaseSep2 compares to NonPhaseSep, i.e. the equivalent of Fig. S7. Please discuss thoroughly which scenario is more likely correct. What effect does the addition of LLPS have on the simulation results?

Minor comments

l. 114-116 – What's the point of this reference in this context? "Low" and "high" are obviously relative. Also, please specify what is meant with "remaining bulk".

l. 126 – Where is the amplification? Amplified compared to what?

l. 169 – What do you mean with "particles [. . .] can only dissipate energy by rebounding". Are you talking about particle bounce measurements? How is this connected to the cited "almost full resistance to reactive uptake"? Please fill in the connections between these concepts.

In equation (3), l. 205, the sum of w_a, w_b and w_s is not 1. Is this intended?

l. 367 – "This indicates that anthropogenic species have a higher range of glass transition temperatures than biogenic species" – The "range" is larger for biogenics, you probably want to point out the overall higher values. Same in l. 402.

l. 399 – How is a bimodal distribution relevant for Fig. 2?

l. 419 – How is reduction of water connected to disappearance of bimodal $T_{g,org}$?

Please explain.

Fig. 4A – What is the black line at the bottom of the plot representing? Panels of Fig. 4 do not appear in the order they are presented in the manuscript.

l. 474 – “This suggests that anthropogenic aerosol components are likely more water soluble than biogenic components.” - Do you have more than statistical evidence for that? Shouldn’t that be easy to derive from model input rather than from model output.

l. 486 – “Some mismatch can be attributed to the lack of an explicit mechanism to compute organic aerosol water uptake and some unaccounted SOA formation mechanisms.” - Please expand on this, how would you attribute these to mismatch? Does the data make you recognize this or are these just general shortcomings of the model?

l. 492 – “The difference in observed and model estimated Torg:T range was statistically significant with a P-Value = 0.001” - What does this entail? You are testing the hypothesis that both data sets (model/field) are different. Why?

l. 500 – “Wider ηorg ranges at higher RH can be explained by increased diffusivity with higher aerosol liquid water in SOA causing quick mixing times often accompanied with drastic differences in composition” – Can you expand on this claim (i.e. drastic differences in composition) and back it up with data? I would think high variance in η_{org} at 80 % RH is simply due to a very steep η(RH) curve in that humidity range.

l. 508 – “This can be attributed to shattering of highly viscous SOA ($\eta_{org} \geq$ 106 Pa•s) for RH $\leq$ 30% that inhibits their flow in laboratory measurements of η_{org}.” - Explain how the shattering of SOA in these studies causes a general overestimation of viscosity. To my knowledge, the authors of these papers tried to account for shattering in their viscosity prediction. Is this really the only source of deviation? This would be a good place to talk about idealized laboratory SOA and field samples.

Fig. 8 – Different color scheme for panels a and b is misleading. Caption text denotes that biogenic SOA mass is primarily driven by IEPOX SOA, which according to panel b

is clearly not the case.

Technical Comments

Plase standardize the use of “O:C”. O:C is sometimes in parenthesis, sometimes not. O:Cavg can be misunderstood in way that only the carbon part is averaged.

Math equations in this manuscript appear overall messy, especially due to long italicized words.

Multiple inaccurate multiplication symbols are used: *, •. Please use ·.

Check use of italic vs. non-italic symbols for variables is not consistent throughout the manuscript (kb and T should be italicized in l.182, equation numbers are sometimes in italics sometimes not etc.).

“Tg can determine when aerosols are in a highly viscous glassy state” is a colloquialism.

l. 78-82 – Please revise too long sentence.

l. 117 – What does “pathways that typically happen in the ambient conditions” mean? Are there other pathways that happen under other conditions? Please be specific.

l. 120 – Extra white space before comma. Reference missing?

l.124 – Check subscript of D_{org}.

l. 158, 160 and elsewhere – Consider changing the shorthand “phase” to the more proper “phase state” in this manuscript about phase separation.

l. 176 – “Criteria” is plural, so this should be either “criterion” or “were applied”.

l. 202 – superfluous comma

l. 204 – “adds” should be “add”

l. 215 – There seem to be formatting issues in lines 212 and 215.

l. 295 – Eq. (14) should read Eq. (15).

l. 308 – I would refrain from using the casual “off of” in a scientific paper.

l. 339 – I suppose “chromatogram” should read “chromatography” or “chromatograph” here.

l. 341f – The term OA (organic aerosol) is misused in this paragraph. It appears you talk about molecules, yet you refer to speciation of particles.

l. 359 – “of” missing?

l. 522f – Do you really know these numbers to four significant digits?

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-900, 2019.