

Interactive comment on “Competition between water uptake and ice nucleation by glassy organic aerosol particles” by T. Berkemeier et al.

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Referee comment 1:

Recently researchers have suggested that glassy secondary organic aerosols can cause ice nucleation. However, it is still not clear if these particles act as ice nuclei under atmospheric conditions because the processes involved are numerous and complex. In this manuscript the authors have come up with an elegant way to model these processes. Confidence in the modelling approach was gained by comparing model results with recent laboratory results. Then, model results were used to predict atmospheric conditions that may lead to ice nucleation by glassy secondary organic aerosols. The paper represents a substantial contribution to scientific progress on the

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topic. I expect this study will motivate future laboratory studies to constrain better some of the physical parameters needed for modelling ice nucleation on glassy secondary organic aerosols. I highly recommend this paper for publication in ACP after the authors have adequately addressed the following comments.

Response:

We thank anonymous referee 1 for her/his very careful study of the manuscript and we are pleased about the very positive evaluation. We will address all the comments and helpful suggestions in the revised version of the manuscript. We will clarify especially the presentation of uncertainties in the model calculations and discuss how they relate to uncertainties in model input. The very detailed specific and technical comments are highly appreciated and will all be implemented upon revision. In the following, we list point-by-point responses to the referee's comments.

Referee comment 2:

General comments regarding uncertainties in the calculations: Figure S4 shows FDRH of four different SOA precursors as well as their quasiequilibrium glass transition, with uncertainties represented by shaded bands. For clarity and ease of reading, it would be helpful to state in the figure caption the source of the uncertainties (i.e. what uncertainties are considered in the figure). I assume the uncertainties come from uncertainties in $T_{g,org}$, k_{GT} and κ_{org} . Two sets of uncertainties are reported in the manuscript. The first set (shown in Figure S4) uses $k_{GT} = 2.5 \pm 1$. The second set of uncertainties (shown in Figure S6, orange shaded) includes a wider range of k_{GT} . From the document I could not tell which set of uncertainties is most applicable to the present modelling studies. Please clearly discuss which set of uncertainties is most applicable to the present modelling study and justify. This may have been discussed in Koop (2011), but additional discussion in the current manuscript would be very helpful. There are large uncertainties in calculated FDRH when all the parameters are taken into account (see Figure S6). These uncertainties should be mentioned in the conclu-

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sions and perhaps the abstract. In addition, it may be helpful to the community if the authors gave some directions on measurements that are needed to help reduce the uncertainties.

Response:

This is correct, the uncertainties in Fig. S4 come from input parameter uncertainty. We admit that our discussion of model output uncertainty might have been confusing. Fig. S4 and Fig. S6 both use the respective input parameter uncertainties indicated in Table A1. While Fig. S4 shows the comparably small uncertainties within a certain SOA class, Fig. S6 shows the overall uncertainty that arises when using the very broad SOA ‘best guess’ in Koop et al. (2011). This ‘best guess’ did not distinguish and resolve the various precursor types. Figure S6 was thought to highlight which changes are induced by which input parameter. We agree that this was somewhat confusing and not well described. We will add proper references to Table A1 and an improved description to the caption of Fig. S4. Furthermore, we have completely redesigned Fig. S6. We added a new section 3.4 to the manuscript describes the uncertainties associated with model input. In this section we also give directions on future laboratory measurements.

Referee comment 3:

Page 16473, line 15-20. If the uncertainties in the model predictions are considered, are the freezing results above 230 K still inconsistent with the model predictions?

Response:

If the uncertainties in the model predictions are considered, a few of the data points can be explained, but the majority cannot, they significantly lie outside the predicted FDRH range. In fact, the sensitivity of FDRH to all model input parameters (T_g , k_{GT} , K_{org}) becomes very low when FDRH approaches water saturation. At a certain point, it is not possible to further lift FDRH towards the water saturation line anymore since

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the curvature of the aw curve is very steep there (composition of the deliquesced shell changes quickly with increasing RH, thereby increasing the diffusion gradient of water). We will add a sentence to Sect. B2 that discusses a potential reason for the deviation between model and experiment:

Possibly, insoluble products from Naphthalene OH oxidation remained solid in the otherwise fully deliquesced particle and nucleated ice heterogeneously with lower efficiency. Such a process is not considered in the model, which does not resolve single compounds and treats Naphthalene SOA as homogeneous mixture at all times.

Referee comment 4:

Other general comments: Page 16461, line 20-25. Full deliquescence relative humidity (FDRH) is defined as the point where the entire particle is homogeneously mixed and its water activity corresponds to that of a liquid (i.e. it is larger than that of the quasi-equilibrium glass transition). Why is the constraint of “entirely homogeneously mixed” needed? I can image a case where the water activity corresponds to a liquid everywhere in the particle, but the particle is still not homogeneously mixed due to slow diffusion in the liquid. Does this situation ever arise?

Response:

This situation indeed arises in the simulations when the trajectory starts slightly above the nominal glass transition (e.g. 229 K for sucrose particles). At model runs with these starting temperatures, all features of the kinetically limited deliquescence of a glassy particle can be observed even though the particle is formally non-glassy (sharp water diffusion front, etc.).

Referee comment 5:

Specific comments: Page 16461, line 5: I believe it should be “from” instead of “form”

Response:

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This will be changed in the revised manuscript.

Referee comment 6:

For alpha-pinene are the authors using proxies corresponding to ozonolysis or OH oxidation. Please specify for clarity.

Response:

The model studies we referred to were simulating α -pinene SOA from dark ozonolysis (Shilling et al., 2009; Zuend and Seinfeld, 2012). The substances found in field measurements (MBTCA, terpenylic acids) could be formed by either photooxidation and ozonolysis. This was clarified in Sect. A2, which now reads:

The group “ α -Pinene” contains compounds characteristic for photooxidation and ozonolysis of the biogenic SOA precursor α -pinene, which has been chosen as proxy for the different monoterpene VOCs responsible for biogenic SOA formation.

Referee comment 7:

Page 16462, “Ice nucleation regimes”: Through the section, please reference the up-draft velocity and the corresponding type of clouds, when possible (e.g. at page 16462, line 19).

Response:

We will reference the paper of Jensen et al., ACP (2005) at all three instances in the revised version of the manuscript.

Referee comment 8:

Page 16467, line 14: Should “latitude” be replaced with “altitude”.

Response:

This will be changed in the revised manuscript

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Referee comment 9:

Figures: All figures. Please indicate what size of droplets the homogeneous freezing line corresponds to.

Response:

The homogeneous freezing line is a model result as described in Sect. 2. As particles increase in size during the humidification process, the size of the droplets at the homogeneous freezing line is not a constant. In Fig. 2B and Fig. 3A, this would lead to multiple hom. freezing lines that are undistinguishably close. For these two figure panels we used the homogeneous freezing line obtained for 100 nm sucrose particles, humidified at a rate of 1 % RH min⁻¹. Since in these figures the hom. freezing line functions only as a reference point and the induced error is very small, we decided to not dwell on this simplification in the figure caption.

Referee comment 10:

Figure 1 caption: I believe there is a typo for “typical”.

Response:

This will be changed in the revised manuscript.

Referee comment 11:

Supplement: Table S1, column 1. References are not properly formatted. For example see “Kautzman 122”. Also there is some nomenclature in this column that is not defined. For example what does “CARB” represent.

Response:

We apologize for the inconsistent nomenclature in Table S1. We tried to adopt most compound names from the original publications. We will clarify this with a number of additional footnotes explaining the origin of the specific compound name.

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Referee comment 12: I can't see Table S3 mentioned anywhere in the text (either main text or supplemental). Please discuss somewhere how these parameters are used.

Response:

The reference in I.54 was erroneously pointing toward Fig. S2, but should have pointed toward Fig. S3. This will be changed in the revised manuscript.

Referee comment 13:

Line 52: ("cf figure") give a number to the figure if possible.

Response:

We will include the reference to Figure B2 in the revised manuscript.

Referee comment 14:

The caption of Table S2 does not appear to be consistent with the data in the table.

Response:

We hope we can resolve the confusion by redirecting the earlier mentioned reference from Table S2 to Table S3 (see response to comment 12).

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 16451, 2014.