

## ***Interactive comment on* “State transformations and ice nucleation in glassy or (semi-)solid amorphous organic aerosol” by K. J. Baustian et al.**

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The authors would like to thank the reviewers for their careful reading and helpful suggestions regarding this manuscript. At the suggestion of both reviewers we have now included a discussion of particle viscosity and timescales for water diffusion into the micron-sized (semi-)solid particles. Theoretical  $T_g(\text{RH})$  curves following the methods of Koop et al., 2011 have also been added to state diagrams. They are in good agreement with  $T_g(\text{RH})$  curves fit to experimental water uptake data and lend support for the hypothesis that there may be a relationship between water uptake and  $T_g(\text{RH})$  that could be used to predict partitioning between organic aerosol phase states. Through-

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out the manuscript we have streamlined and clarified terminology. Detailed responses to referee #2 are outlined below and where necessary changes have been incorporated within the manuscript.

#### Anonymous Referee #2:

In the work on hand, three compounds considered surrogates for secondary atmospheric aerosol (SOA) are investigated experimentally upon their behavior toward water uptake and ice nucleation under atmospherically relevant conditions. Furthermore, mixtures of these organics with ammonium sulfate are described to increase significance of the conclusions for actual chemical compositions in the tropical tropopause layer (TTL). Therefore, the submitted manuscript is clearly within the scope of ACP and the title clearly reflects its contents.

The combination of optical microscopy, raman spectroscopy and application of the CARMA model provides a very complete consideration of the topic and all employed methods can be followed reasonably well. The data presented in this study leads to nice quantitative conclusions for the relevance of heterogeneous ice nucleation on glassy aerosols in atmospheric conditions, which are substantial enough for publication. As not indicated otherwise in the specific comments, the paper is well written in a clear and concise fashion. I therefore recommend the paper for publication, but have a few points of critique that need to be addressed.

Besides some minor points (see specific comments), my main points of critique are the lack of consideration of diffusional limitations to the deliquescence process and the very indirect way of inferring glass transition values.

#### Response from Authors:

The authors agree, that the manuscript would be improved by the addition of a discussion of diffusional limitations to the amorphous deliquescence process. Calculations of particle viscosity and timescales for water diffusion into the micron-sized sucrose

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particles investigated in this study have been discussed in detail in the response to reviewer 1 and have now been added to Section 3.2.

For aerosol glasses, the nature of the system sometimes requires the use of indirect methods to probe thermodynamic or dynamic changes in aerosol particles that may be indicative of the glass transition. Other indirect methods are used that take advantage of properties of glassy materials, for example, glasses shatter, and as a result, mechanical processes to crack/shatter aerosol particles have been used to demonstrate their phase. Solid particles are more likely to bounce off surfaces than liquid particles, and as a result, the fraction of particles that bounce has also been used as a metric for particle phase state (Virtanen et al., 2010; Saukko et al., 2012). Interaction of the aerosol particle with water vapor is an indirect measure of particle viscosity and therefore, similar to other indirect methods employed.

In this paper, we originally sought only to measure the onset of water uptake and ice nucleation, but later noticed the data seemed to be tracing a curve that resembled a glass transition curve. Good agreement between the experimental data presented and the theoretical  $T_g(\text{RH})$  curves generated using the approach of Koop et al., 2011 lend further support for this hypothesis. (Discussion added to section 3.3).

Anonymous Referee #2:

In this manuscript, water uptake is assumed to occur simultaneously with glass transition and used to build up the glass transition parameterization. This might be misleading in several ways which should at least be indicated in the paper: As mentioned in I. 5-11 on page 27346, the uptake of water depends on the actual humidification rate (and furthermore on other parameters such as particle size) so that the reported water uptake onset should be considered as an upper limit for the water uptake onset under full equilibration conditions (infinitely slow change in RH). Especially at very low temperatures, this might (in part) explain why values measured by Zobrist et al. (2008), consistently lie at lower temperatures.

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## Response from Authors:

In the updated manuscript we have further emphasized that the glass transition is highly dependent on humidity and have been careful to use the notation  $T_g(\text{RH})$  throughout the manuscript as a reminder that we are investigating the glass transition as a function of RH which is fundamentally different than  $T_g$  that is not influenced by humidity. Thus, in the interest of obtaining the results most relevant for atmospheric applications, we have employed RH ramp rates that reflect rates found in the upper troposphere. Additionally in section 3.3 we have noted that the onset water uptake may be an upper limit because RH for water uptake is expected to decrease as the humidification rate is decreased towards zero (full equilibrium conditions). Theoretical predictions of  $T_g(\text{RH})$  based on the methods of Koop et al. 2011 have also been added to figures 2, 3, and 4. Swathes calculated the Koop et al. approach are in good agreement with the experimental data presented and lend further support that the Raman method may be used to estimate  $T_g(\text{RH})$ .

## Anonymous Referee #2:

$T_g$  values in Zobrist et al. (2008) were determined calorimetrically, thus following the thermodynamic definition of a glass! The thermodynamic and kinetic definitions of the glass state are not the same and it is furthermore still unclear how the permeation speed of water behaves as function of the viscosity of the organic matrix. For both reasons, it is doubtful that water uptake onset and glass transition of the organic matrix coincide in a deliquescence experiment. I would suggest working out the differences in both methods of  $T_g$  determination a bit more and you may want to point out what assumptions go into your proposed values for  $T_g$ .

## Response from Authors:

There are multiple ways to probe glass formation- probing heat capacity through calorimetry or indirectly through dynamic measurements. So far, all methods that have been used for aerosol particles have some limitations. Water uptake is a proxy for diffu-

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sion timescales within a particle and therefore can be used to indicate particle viscosity, a widely recognized [Debenedetti and Stillinger 2001] indirect method for determining  $T_g$ .

Comparison of our  $T_g(\text{RH})$  values to  $T_g$  values from Zobrist et al. (2008) have been removed from the final version of the manuscript because a humidity-forced glass transition is fundamentally different and should not be compared to non-humidity forced measurements. In the final version of the manuscript we have added additional support for our findings by including an estimation of the timescale for water diffusion into a glassy or semi-solid matrix using the methods of Zobrist et al. 2011 and also through theoretical calculations of  $T_g(\text{RH})$  [Koop et al. 2011] for the pure organic substances. (Sections 3.2 and 3.3)

Anonymous Referee #2:

To correctly discuss Fig. 1 it might be helpful to plot the “state diagram” in  $T$  vs. water activity ( $a_w$ ) space to omit the problem of non-equilibrium aerosol particles or alternatively point out that the particle has to be in full humidification equilibrium to adopt the state suggested by the state diagram.

Response from Authors:

Figure 1 has been removed from the final version of the manuscript and the explanation of state diagrams has been moved to the first paragraph of section 3.2

Anonymous Referee #2:

Specific comments

p. 27336, l. 16ff - This sentence implies that Debenedetti and Stillinger (2001) treated glassy solids in the context of atmospheric aerosol, which is not the case.

Response from Authors: This sentence has been changed.

Anonymous Referee #2:

p. 27337, l. 8 - What do you mean with “natural” aerosol particles?

Response from Authors: The authors agree that the use of “natural” here is unclear. It has been changed to “atmospheric” to reflect the fact that these studies examined aerosol collected from the ambient atmosphere, as opposed to aerosol proxies.

Anonymous Referee #2:

p. 27340, l.20 - It is not clear to the reader what feature in the C-H-stretch signal at 2900-3100  $\text{cm}^{-1}$  can lead to distinction of glassy and crystalline organics. It is neither obvious from Fig. 2, nor is it used for distinction later in the text.

Response from Authors: Raman spectra of crystalline citric acid, for example the bottom spectrum shown in the left panel of Figure 1, have distinct sharp peaks in the O-H and C-H stretching region between 3100-3600  $\text{cm}^{-1}$  and 2900-3100  $\text{cm}^{-1}$ . In contrast, Raman spectra of amorphous citric acid particles (bottom spectrum in the right panel of Figure 1) have only broad peaks in these same regions. This peak broadening occurs due to the disordered nature of O-H and C-H bonds in an amorphous species compared to the well-ordered crystalline solid. A similar description has been added to section 2.1.

Anonymous Referee #2:

p. 27344, l. 18f - Please indicate again how exactly liquid water was observed here, I guess raman spectroscopy?

Response from Authors:

Raman spectroscopy was used to detect uptake of liquid water on particles in this instance. This has been made clear in section 3.2 of the updated version of the manuscript.

Anonymous Referee #2:

p. 27344, l. 21ff - If the glass transition values at 0 % and 100 % RH have been

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weighted differently than the other experimental values in the polynomial fit, please indicate this. Glass transition values normally follow a Gordon-Taylor relationship (see e.g. Zobrist et al. (2008), Koop et al. (2011)), have you tried to do the fitting following this approach? This could be helpful for the comparability of your study to existing studies.

Response from Authors:

The values at 0% and 100% RH were weighted the same as the experiment data points shown and this has now been stated in the text.

The Gordon-Taylor approach along with data from Zobrist et al. 2008 and formulations from Koop 2011 have now been used to plot theoretical  $T_g(\text{RH})$  curves that have been added to the discussion in section 3.3 and figures 2, 3 and 4 in the final manuscript. The theoretical approach put forth by Koop 2011 is in good agreement with experimental data for the onset of water uptake on the particles.

Anonymous Referee #2:

p. 27345, l. 1 - Please make more clear that this only the case after full equilibration with the surrounding air, which must not be the case at humidification rates of 0.1 % RH/min, especially at very low temperatures due to diffusion limitations. It would be correct in any case if the state diagram would be T vs. aw.

Response from Authors:

This sentence has been expanded to make it clear that equilibrium conditions were an underlying assumption.

Anonymous Referee #2:

p. 27346, l. 19 - Where do you find this value in Wang et al. (2012)? They found rather  $\approx 85\%$  RH or  $\approx 115\%$  RHice.

Response from Authors:

The authors apologize for the confusion this caused. In this instance we had listed the difference between our results and theirs at 240K ( $\sim 15\%$ ). The value has now been changed to 85%, reflecting the actual value shown in Wang et al. 2012. (Section 3.5)

Anonymous Referee #2:

p. 27348, l. 17ff - Wang et al. find heterogeneous nucleation onsets of  $S_{ice} > 1.35$ . This is a significant deviation to the values in this study ( $S_{ice}=1.2-1.4$ ) that I find worth mentioning.

Response from Authors:

Yes, Wang et al. 2012 report mean ice onsets for deposition freezing between  $S_{ice} = 1.36$  and  $1.52$  (shown in Wang, figure 2). However, they also note that onsets for individual experiments were as low as  $S_{ice} = 1.23$  were observed, but not shown in their figure 2. Additional discussion regarding comparison between these studies has now been added.

Anonymous Referee #2:

p. 27348, l. 28ff - In this sentence it is hard to understand what exactly can be explained by competition between water uptake and ice nucleation. Please reformulate. Does competition occur between particles or for every individual particle? You could also mention the possibility of a potential immersion freezing here.

Response from Authors:

The word competition was confusing in this instance. Immersion mode freezing would have occurred if water uptake and ice formation were observed on the same particle. In the case of the experiments discussed here, water uptake and ice formation were observed on different particles. As stated in the manuscript, we could not rule out immersion mode freezing when both water uptake and ice are observed at once. Experiments in which both water uptake and ice were observed always occurred at experimental conditions corresponding to a special region of the state diagram where

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the RH needed for water uptake was nearly the same as RH (or Sice) where ice formation was anticipated. So it is also possible that we were observing a competition between the two processes (i.e. freezing versus water uptake). We have expanded the discussion in the section to make these points more clearly.

The term “simultaneously” may have been misleading here. The phrase was intended to mean that both water uptake and ice were observed at nearly the same time on separate particles. With our experimental setup it was not possible to determine precisely which occurred first. At warmer or colder temperatures where one process clearly dominates this is not a problem. The experimental points have been given their own color to make it clear that the results were distinct for these experiments and we have emphasized that either depositional or immersion freezing may have occurred in these instances.

Anonymous Referee #2:

p. 27349, l. 6 - Which paper is meant here, Wang et al. still? Please make this clearer.

Response from Authors:

We were actually referring to the data presented in the present study. This has been made clear in the text now.

Anonymous Referee #2:

p. 27349, l. 8f - What exactly is similar in the ice habit? This would be worth mentioning if it can be explained in 1-2 sentences.

Response from Authors:

The authors felt that it would not be easy to explain this in 1 to 2 sentences so we have removed this sentence from the manuscript.

Anonymous Referee #2:

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p. 27351, l.10 - Liquid and amorphous don't exclude another. What you mean is "either liquid or (semi-) solid amorphous".

Response from Authors:

Yes, this sentence has been changed in the text.

Anonymous Referee #2:

Fig. 1 - Why does the experimental trajectory bend off? This is not explained in the text.

Response from Authors:

In the final version of the manuscript Figure 1 has been removed, however, the "kink" or change in slope in the former Figure 1 was meant to reflect the two different cooling rates that were used in each experiment.

Anonymous Referee #2:

Fig. 2 - The exact onset cannot be determined from the diagrams. I'd suggest adding figures with spectral subtraction data as supplementary material.

Response from Authors:

As suggested a panel depicting spectral subtractions for Figure 1 has been added in Appendix A as Figure A1.

Anonymous Referee #2:

Technical corrections

p. 27339, l. 13 - Consider writing "glass transition curve (T<sub>g</sub>, blue)" for consistency inside the sentence.

p. 27346, l. 19 - Here it should be "onsets" instead of "onset".

p. 27343, l. 15 - I find "dramatic" too strong here.

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Response from Authors:

These technical corrections have been made.

Anonymous Referee #2:

Table A1 - Denotation “A1” is usually used for tables in the appendix, consider changing it to “1”. First column: Consider using substance(s) instead of substance.

Response from Authors:

Table A1 is part of Appendix A so the notation was retained.

Anonymous Referee #2:

Figs. 3 to 5 - Right panels contain a lot of blank space, consider changing y-axis range to Size=0.8 - 1.8.

Response from Authors:

Changing the scale from 1.8 to 2 did not significantly change the appearance of these graphs and the authors opted to leave them as they were.

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 27333, 2012.

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