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Atmospheric Chemistry and Physics Discussions

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 Tg(RH) curves following the methods of Koop et al., 2011 have also been added to state diagrams. They are in good agreement with Tg(RH) curves fit to experimental water uptake data and lend support for the hypothesis that there may be a relationship between water uptake and Tg(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 each of the referee's comments are outlined below and where necessary changes have been incorporated within the manuscript.

Anonymous Referee #1 This manuscript describes an experimental study investigating the water uptake and ice nucleation ability of aqueous organic and inorganic/organic particles in various amorphous phases such as semi-solid and glassy states. Sucrose, citric acid, and glucose species were employed as surrogates for atmospheric secondary organic aerosol (SOA) and ammonium sulfate as inorganic material. Raman spectroscopy was applied to determine respective glass transition points and optical microscopy for detection of ice nucleation. Glass transition points as a function of relative humidity (RH) and temperature (T) were determined and ice nucleation onsets as a function of ice supersaturation, Sice. It is found that amorphous organic particles nucleate ice for Sice between 1.1–1.4 for 235–200 K. Addition of ammonium sulfate to the organic particle causes the particles to remain liquid over a greater temperature range and resulted in ice nucleation onsets of Sice = 1.25–1.48. The glass transition curves are implemented in the Community Aerosol Radiation Model for Atmospheres (CARMA) to estimate the fraction of glassy aerosol in the middle upper troposphere and tropical tropopause region. Overall this manuscript reads well and the topic fits nicely within ACP. The experiments are based on previously established methods and setups. In this regard I have no reservation to recommend the manuscript for publication. However, I have some comments regarding the data analysis, interpretation and model application which need to be addressed before the manuscript can be recommended for publication. Throughout the manuscript more care should be taken in regard to the definition of the particle phase states. For example an amorphous particle can be liquid, semi-solid, or glassy. So "glassy or amorphous (semi-)solid organic particles" is an incorrect expression. What are aqueous organic glass particles? Within the glassy matrix some water molecules will be incorporated, however, it is doubtful to define this particle as aqueous in the common sense. It may be better to write glassy organic or glassy organic/water particle. There are many of these types of ambigu-

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ous/incorrect definitions which should be corrected (e.g. “as highly viscous (semi-) solids in amorphous or glassy states”).

Response from Authors: The authors apologize for any confusion that was caused regarding various terms used to describe particle phase throughout this manuscript. We believe part of the problem is that there is no standard terminology within the literature right now. For examples, the term “(semi-)solid amorphous” was adopted from Mikhailov et al., 2009 who used the phrase to describe both glasses as well as rubbers, gels, ultra-viscous or highly viscous liquids (all semi-solids). Wang et al., 2012a, referred to particles as “amorphous secondary organic aerosol” throughout their manuscript. The term “aqueous organic glass” was used by Zobrist et. al. 2011 to describe aerosol particles that consisted of binary mixtures of sucrose and water. Bones et al., 2012 has chosen “binary aqueous sucrose particles”.

The authors agree with the reviewer that the use of one consistent terminological convention would add clarity to the manuscript. For that reason in the updated version of the manuscript we now refer to our samples in a general sense as “amorphous (semi-)solid aerosol”. Where possible we now reference specific phase states using the terms “glassy”, “semi-solid” or “liquid aerosol”. We have also defined these terms in the introduction to clarify the terminology.

Anonymous Referee #1: A major point of discussion which is lacking in this manuscript is in regard to particle size, viscosity, and time scales to achieve water diffusion throughout the particle (Shiraiwa et al., 2011). These parameters are crucial when comparing experimental results with other studies and for application in models.

Response from Authors: The authors agree, the manuscript would be improved by the addition of a discussion of viscosity and time scales for water diffusion into the micron-sized particles investigated in this study. This discussion has now been added to Section 3.2. Following the method of Wang 2012a timescales for water vapor diffusion into particles and their viscosity were calculated for pure sucrose particles. Sucrose is the species with the highest Tg(dry) investigated in this study and therefore calculations represent an upper limit for the time scale of water vapor diffusion and viscosity for particles examined. Zobrist et al. (2011) equations 5, 11-13 were used to estimate DH2O over a range of conditions. Characteristic timescales for bulk diffusion into the particles was obtained following the methods of Shiraiwa 2011 (Time =d2/4pi2DH2O). Finally, viscosity of the particles was estimated using the Stokes-Einstein equation which relates particle viscosity and DH2O.

DH2O calculated at the onset of water uptake was found to be on the order of 10-12 cm2s-1 for all sucrose water uptake experiments (T > 236 K). These diffusion coefficients correspond to bulk diffusion timescales on the order of hundreds to thousands of seconds (8 to 34 mins) across the range of T and RH conditions for water uptake by 4 micron sucrose particles. These results indicate that deliquescence of the particles could occur on timescales relevant for cloud-modeling. Viscosities derived at the onset water uptake for sucrose were all on the order of 103 Pa s.

Anonymous Referee #1: Furthermore, it should be emphasized that the glass transition curve does not represent a phase transition curve but will depend on the rate of change in RH and T. Experiments applying different conditions may obtain different glass transition points. The atmospheric time scales with respect to changes in RH and T might be different again. For example the size of the citric acid particles employed by Murray et al. is 150 nm whereas the particles here are up to 10 μm in diameter. Looking at Koop et al. the mixing time scale τ (which leads to liquefaction/deliquescence of the particle) at around 220 K differs by an hour to a year for smaller and larger particles. So, one would not necessarily assume to obtain the same results for water uptake and/or ice nucleation onsets. The Murray et al. study uses much faster cooling rates at cirrus conditions compared to this study. Maybe the different experimental conditions may result by chance in similar results. Clearly more discussion is needed regarding these points.

Response from Authors: In the interest of obtaining the results most relevant for atmospheric applications, we have employed experimental temperature and RH ramp rates that reflect rates found in the upper troposphere. Although there are variations in RH ramp rate, aerosol composition and particle size between various studies, the fact that experimental results from this study and others (e.g. Wilson et al, Wang et al., etc.) all fit within the range of Tg(RH) values for SOA from Koop et al., 2011 is positive evidence that these various studies are all valid and comparable.

In the final version of the manuscript we have further emphasized that the glass transition is highly dependent on humidity and have now clearly defined Tg(RH) to emphasize the fact that we are reporting glass transitions as a function of RH which is fundamentally different than a Tg in a dry environment. Additional discussion has also been added to section 3.3 regarding the comparability of various studies.

Anonymous Referee #1: Having said this, I am not sure how meaningful the modeling results are since dynamics, i.e. convection and diffusion time scales, governed by particle size are not considered. Here, only if T is below or above Tg, determined from particles 1–2 orders of magnitude larger than in the atmosphere, the glassy or liquid state, respectively, is inferred. Smaller atmospheric particles will need less time to transform from a glassy to liquid state. As is, the model may be biased towards solid particles? In general this application needs more explanation and maybe elaboration of the model.

Response from Authors: Dynamics, including convection, RH and T were included as part of the modeling study. The dynamical framework employed reflects temperature and RH changes from actual parcel trajectories found in the mid-latitude and upper troposphere.

Smaller particles would require less time to undergo amorphous deliquescence however, within particle size ranges from nm to microns the timescale for humidity-induced diffusion of water into this type of particle is typically relatively short compared to the particle lifetimes in the atmosphere. For example, following the methods of Shiraiwa

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et al. 2011 discussed above, a 4 micron particle sucrose particle at 236 K and water activity of 0.709, the timescale for diffusion is ∼22 mins versus 1.4 mins for a 1 micron particle at the same conditions. Since we use 3-8 micron particles for water uptake experiments our modeling results may represent an upper limit for the fraction of time glassy particles can be expected. However, state transitions are expected to occur on atmospherically relevant timescales.

That said, we have reported values for the onset of water uptake in the glassy particles rather than full liquefaction. Because the Kelvin effect will have a small role for particles larger than ∼ 200 nm, the onset of water uptake may be similar for particles of various sizes given similar conditioning.

Part of the reason for incorporating the Koop at al. 2011 SOA curves as part of our discussion and modeling simulation was to produce results that would be relevant for a range of different particle types, conditioning and sizes, even if there were biases due to the specific experimental parameters or particle sizes investigated in this study. The good agreement between the Koop et al. 2011 method, our experimental results and the experimental results of other groups lends support for the case that results are atmospheric relevant.

Therefore, we believe the model results presented here reflect the best possible estimates given all available data and experimental results. We hope that this initial modeling study serves to motivate further discussion on the topic of glassy aerosol and that our work can be used as a jump-off point for further more complex modeling work once further data becomes available.

Anonymous Referee #1: I think Saukko et al. deserves more reference in the introduction since they investigated how addition of sulfates to organic aerosol affects Tg. Also, the study by Wang et al. which shows derived Tg from complex 'real' SOA particles (no single component surrogates) and ice nucleation onsets deserves more reference since the other studies mostly investigate simpler particle system. It seems that the

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Wang et al. Tg is on the upper end of the estimated range by Koop et al.

Response from Authors: Further discussion of these two studies has been added to the paper as per the reviewer's suggestion.

Anonymous Referee #1: Derivation of glass transition curves. As outlined by Koop et al. there have been physical/semi-empirical descriptions of Tg. Those are employed in many different fields rather successfully and form the base for the Koop et al. Tg estimation. It seems also to work for the SOA particles studied by Wang et al. So, why are the Tg curves here just described by a polynomial fit fixed at RH =100 and 0%? The extrapolation of these fits beyond the data may not be correct. Would the Gordon-Taylor description of Tg predict similarly lower Tg when adding ammonium sulfate?

Response from Authors: At the outset of experimentation we did not expect water uptake results to trace the shape of a glass transition curve and thus we had proceeded by using polynomial fits to the data. As the reviewer points out, the Gordon-Taylor approach and other physical/semi-empirical descriptions of glass transition curves have been used in the past for similar experiments. As per the reviewer's suggestion we have added theoretical Tg(RH) curves to our state diagrams following the method of Koop et al. 2011 which in turn relies upon formulations from Gordon-Taylor. Figures 2, 3, and 4 now include the calculated Tg(RH) swathes based method outlined in Koop et al. 2011.

Examination of Figures 2, 3, and 4 show that theoretical Tg(RH) swathes calculated using the Koop et al. 2011 approach are in good agreement with the experimental data presented and lend further support that the Raman method may be used to estimate Tg(RH).

Polynomial curves fit to experimental data are very similar to theoretical Tg(RH) swathes and have therefore been retained for use in the model as the authors preferred to present results based on both empirical and theoretical (the Koop SOA swath) modeling results.

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Anonymous Referee #1: Specific comments: p. 27337, l. 7–10: You could mention a new study by Shiraiwa et al. (2012) who looked at chemical aging of glassy levoglucosan by NO3.

Response from Authors: This reference has now been added to the introduction.

Anonymous Referee #1: p. 27337, l. 20: Deposition ice nucleation occurs from the supersaturated vapor phase.

p. 27337, l. 22: Immersion freezing occurs from a supercooled aqueous droplet.

p. 27337, l. 23: Contact freezing occurs from a collision of an ice nucleus with a supercooled aqueous droplet.

Response from Authors: We have changed our descriptions of the different modes of ice nucleation to reflect the reviewer's suggestions.

Anonymous Referee #1: p. 27338, l. 20: Here but also for the remainder of the manuscript (see below) what is meant by "fraction of time"? I assume it is meant the fraction of all particles which are solid? I don't see a "time dependence" in this analysis. I feel this is an unfortunate expression and should be exchanged in text and figures and more clearly defined

Response from Authors: The phrase "fraction of time" was adopted from previous works (e.g. Wise 2010 and Jensen 2010) by co-author Jensen. "Fraction of time" does not refer to a fraction of aerosol by mass, but reflects the percentage of time an average particle was glassy as the model follows an air parcel along its trajectory through the mid-latitude and TTL region. Since this terminology was adopted from past studies it has been retained, but has now been explained in section 4.

Anonymous Referee #1: p. 27339, l. 24: How do you know that "Water uptake by a glassy or amorphous (semi-)solid substance generally requires higher RH at colder temperatures"? Mikhailov et al., 2009 did not study deliquescence as a function of temperature as far as I recall.

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Response from Authors: The citation for Mikhailov et al., 2009 was meant only to reference to the terminology used in the first half of this sentence (i.e. moisture-induced phase transition and amorphous deliquescence). This sentence has been revised.

Anonymous Referee #1: p. 27339, l. 27: How do you know that “If supersaturation (with respect to ice) is reached before the RH necessary for water uptake, depositional ice nucleation will be observed.” If the particle is not a good ice nucleus than ice nucleation may not occur. This statement is too general.

Response from Authors: We have changed this sentence to reflect that a depositional ice nucleation pathway may be available.

Anonymous Referee #1: p. 27342, l. 2: Define “VPice”.

Response from Authors: A definition has been added.

Anonymous Referee #1: p. 27343, section 3.1: I suggest to show an additional figure of the spectral subtraction since the actual figures do not readily indicate substantial changes due to a phase transition. Also, how is the subtraction performed? Is the raw data subtracted or do you perform a background correction and actually fit the peaks and then subtract the fitted peaks?

Response from Authors: Spectral subtractions for both amorphous and crystalline deliquescence examples have now been added for reference in Appendix A as Figure A1. Raw spectral data was used for subtractions without a background correction however the spectra were normalized using the intensity the C-H peaks prior to subtraction. Further explanation has been added to section 2.1 to detail how spectral subtractions were performed.

Anonymous Referee #1: p. 27345, l. 2–3: Semi-solid is not glassy. Thus liquid and semi-solid should be left of the Tg curve and glassy to the right.

Response from Authors: The reviewer is correct, particles are liquid or semi-solid to the left of Tg and glassy to the right. This has been clarified in the text. (Section 3.2)

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Anonymous Referee #1: p. 27345, l. 5–8: However, water uptake/ice nucleation is determined at temperatures much lower than "ambient temperature". I assume this means about room temperature? At lower temperatures the diffusion coefficient for water in a glassy matrix significantly decreases (Koop et al. 2011).

Response from Authors: Line 8 of this paragraph has been changed to clarify that by "ambient" temperature we meant "room" temperature.

The reviewer is correct, diffusion timescales at temperatures below freezing will be slower than at room temperature. However, humidification increases diffusion timescales by orders of magnitude even at low temperature. This was indicated in line 9-11 of that same paragraph in the original manuscript but the discussion has been expanded for clarity. Calculations of DH2O and timescales for diffusion (as discussed in detail above) have been added to section 2.3 and demonstrate that timescales are on the order of hundreds or thousands of seconds for particles given our experimental conditions.

Anonymous Referee #1: p. 27345, l. 27: What does it mean that the Zobrist et al. data is "shifted slightly"? This and the following discussion may refer to different particle sizes or RH rates as mentioned above.

Response from Authors: In the final version of the manuscript the comparison between our Tg(RH) values and the Zobrist et al. 2008 Tg curves has been omitted because it is not useful to compare Tg(RH) and Tg curves as they are fundamentally measurements of two different processes. (Section 3.3)

Anonymous Referee #1: p. 27346, section 3.4: I feel that the study by Saukko et al. could be included in this discussion. Here only a 1:1 organic to inorganic mixture was studied. However Saukko et al. determined particle phase states for different ratios. Can it be expected that for less ammonium sulfate the particles exhibit a higher Tg?

Response from Authors: The authors have added further discussion of the Saukko

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paper to the introduction.

Yes, you would expect higher Tg(RH) for particles with less ammonium sulfate. Tg(RH) curves for such solutions should fall between the Tg(RH) curve of the pure components and Tg(RH) of the 1:1 mixtures.

Anonymous Referee #1: p. 27348, l. 24–26: Wang et al. determined the phase state at room temperature and RH smaller than 50% to be semi-solid. However, at deposition ice nucleation temperatures the particles are solid. “proposed to be glassy” should be changed to “solid/glassy naphthalene SOA”.

Response from Authors: This change has been made.

Anonymous Referee #1: p. 27348, last paragraph: How can ice nucleation and water uptake be observed simultaneously? This is only possible if immersion freezing occurred. If at a certain RH one particle took up water and another one not, this would imply that the composition of both particles is different. An explanation should be given for this.

Response from Authors: 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. Immersion mode freezing would certainly 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, in these cases we could not rule out immersion mode freezing when both water uptake and ice are observed at once. However, 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 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 water uptake and ice formation processes. We have expanded the discussion in the section. A similar phenomenon was observed by Wise et al., 2012 when investigating deliquescence and ice nucleation by hydrates of NaCl.

At warmer or colder temperatures where one process clearly dominates this is not a problem. The 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 #1: p. 27351, chapter 4: See general comments above on model application. Why was a trajectory of 90 days chosen? The mean residence time of aerosol particles is much shorter. It would be much more meaningful knowing if the particles transform within 1–2 weeks.

Response from Authors: During modeling simulations, a large collection of diabatic back trajectories were launched at 82.6 hPa on a regular grid throughout the tropics and every week for a year. Trajectories were run back 90 days or until they hit convection. Only the subset of trajectories that hit convection prior to the 90 limit were used in this study. The model was then run forward in time from the point of convective encounter to the starting point of the trajectories. At the time of convective detrainment it is assumed that RHice=100%; which sets the initial water vapor concentration in the parcel. If the RHice exceeds 130%, parcel water vapor concentration is reduced to ice saturation. This gives RH along each trajectory. From there, the fraction of time that the parcel temperature was above/below the water uptake curve was used for calculations of the “glassy fraction”. This was not clear in the previous version of the manuscript; we have now added this information to our model description found in Section 4, paragraph 2.

Anonymous Referee #1: p. 27354, l. 6: Only one ice nucleation pathway was discussed in this manuscript, i.e. deposition ice nucleation. The amorphous phase will also dictate water uptake.

Response from Authors: It’s true we only investigated heterogeneous (deposition and possibly immersion mode) ice nucleation in this study. The reference to nucleation

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pathway in this instance was intended to reference the larger categories of heterogeneous versus homogeneous ice nucleation. In this study we aimed investigate how glassy aerosol could affect the partitioning between heterogeneous and homogeneous ice formation pathways and did not attempt to predict how the amorphous phase would specifically influence homogeneous ice formation. However, further studies detailing how glassy aerosol influences homogeneous ice nucleation would also be interesting.

Anonymous Referee #1: Figures 3–5: For which particle size has the Koop et al. parameterization been employed?âĂÍ

Response from Authors: The author's used a homogeneous ice nucleation rate of 5 x 109 cm-3 s-1 which corresponds to a particle radius of ∼0.93 microns to calculate the Koop et al. homogeneous parameterization. The rate used has now been indicated in the text.

Anonymous Referee #1:

Technical correction:

p. 27343, l. 15: Omit "dramatic".

p. 27343, l. 19: Omit "exact".

p. 27343, l. 21: I suggest "up" instead of "on".

Response from Authors: These changes have been reflected in the updated version of the manuscript.

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