

Interactive comment on “Do atmospheric aerosols form glasses?” by B. Zobrist et al.

B. Zobrist et al.

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The authors would like to thank Ben Murray (referee 1) for his constructive comments. We have addressed his concerns point-by-point below.

Scientific concerns:

1) p9265, ln 16-19:

In this section we refer to the aerosol effects in general and not specifically to ice clouds. For clearness we change the sentence on page 9265 ln 16-19 to: "According to the recent Intergovernmental Panel on Climate Change report (IPCC, 2007), the direct and indirect aerosol effects (including only liquid clouds) exert radiative forcings of -0.5 and -0.7 Wm^{-2} , respectively, but exhibit only a low to medium level of scientific understanding."

2)

The ice melting curve, T_m , was extrapolated in such a way that it intersects the glass transition curve, T_g , at the measured glass temperature of the freeze concentrated solution (see the hash in the figure). We note that we cannot determine exactly the concentration of the freeze concentrated solution, but only its glass transition temperature. However, we calculated for each glass transition temperature the corresponding concentration using the Gordon-Taylor equation. Assuming that hexagonal ice formed (see also answer to point 3), the position of the freeze concentrated solution in the state diagram is fixed. To clarify how the dashed and dotted curves are obtained in Fig. 2, we change the figure caption to:

"The ice melting curve, T_m , is from Young (1957), and it is extrapolated to lower temperatures (dashed part) so that it intersects the glass transition curve at the measured glass transition temperature of the freeze concentrated solution (hash). The homogeneous freezing curve, T_{hom} , is a polynomial fit through all data points and the dotted part is an extrapolation to lower temperatures. The glass transition curve is obtained through a Gordon-Taylor fit (see also Section 4)."

3)

The trajectories in Fig. 2 are not purely idealized trajectories, but are based on the experimental DSC measurements. The only exceptions are path B to C in panel e and path E to the ice melting curve in panel f, which is why both are shown as dotted lines. To make this more clear, we add the following sentence to the figure caption of Fig.2: "The colored curves depict the course of the DSC experiments linked to the panel on the left side, e.g., panel (a) is linked with panel (d). The solid lines are based on the DSC measurements, while the dotted lines are idealized trajectories during the crystallization process when no phase equilibrium exists within the samples."

The ice-liquid equilibrium curve from Young (J. Phys. Chem., 61, 616-619, 1957)

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was derived from equilibrium measurements of solutions. Under these experimental conditions, ice is present as hexagonal ice. The ice-liquid equilibrium curve of the metastable cubic ice would be below this curve as stated by the referee, but its exact position is not known to our knowledge. The referee might be right that the solutions shown in the panels c and f do not reach the equilibrium value on the ice melting curve after the cold crystallization, because cubic ice might form. This should be different in panels b and e, where ice freezing occurs at higher temperatures and thus hexagonal ice is likely to form. However, since we cannot derive the crystalline form of the ice from our experiments, and in a recent paper by Murray, ERL, 3, doi:10.1088/1748-9326/3/2/025008, 2008 the ice-liquid equilibrium lines for citric acid/hexagonal and citric acid/cubic ice just differ slightly by about 2wt% at 210 K, we add the following text to the manuscript on page 9269 In 26:

"Note, that T_m depicts the equilibrium line of glucose solutions and hexagonal ice. However, metastable cubic ice might also form implying a slightly lower ice-liquid equilibrium curve might also be applicable in some experiments (see Murray, ERL 2008). Since we cannot determine cubic ice formation in our experiments and due to the lack of data on the exact equilibrium lines of cubic ice and the investigated solutes. Thus we refer to the properties of hexagonal ice in our discussion, which does not restrict any statement in the conclusions."

The referee's comment on mole fraction:

We follow the referee's suggestion by adding a comparison on the mole fraction scale on page 9274 In 8: "A sulfuric acid solution with a concentration of 60.0 wt% corresponds to a mole fraction of 0.355 and a water activity of 0.05 at T_g . A glucose solution with the same mole fraction exhibits a water activity of 0.532 at T_g ."

5)

We replace the sentence on page 9275 In 12-14

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"In the previous section we have seen that organic aerosol constituents seem to have a tendency to form glasses at temperatures and relative humidities relevant for atmospheric considerations."

by the following sentence:

"In the previous section we have seen that organic aerosol constituents seem to have a tendency to form glasses at atmospherically relevant conditions (i.e., temperatures, compositions and relative humidities)."

6)

Hydrophilicity, and thus water solubility, is not a requirement for glass formation. Hydrophobic organic molecules as well as hydrophilic organic molecules form glasses. However, for hydrophilic ones, water is a better plasticizer and reduces T_g more strongly than for hydrophobic ones. Note, that in our statement we refer only to water soluble organics, thus the term 'more hydrophobic' still implies water solubility. To resolve this misunderstanding, we change the corresponding sentence on page 9279 In 1–3 to: "Aerosol particles containing large and moderately hydrophobic water soluble organic molecules are most likely to form glasses at intermediate to high relative humidities in the upper troposphere (UT)."

7)

We investigated the glass transition temperature of the freeze concentrated solution, T'_g , in the same way as was done in previous studies (e.g., Roos et al., Carbohydr. Res., 238, 39-48, 1993; Slade and Levine, J. Food Eng., 22, 143-188, 1994 and also references in these two manuscripts). To our knowledge this is the only way to directly obtain T'_g (apart from extrapolation of the T_m line down to the Gordon-Taylor T_g curve, see point 2 above). We are aware of the fact that this temperature depends on the experimental procedure (e.g., annealing time, annealing rate, as we stated on page 9293 In 3-6, but this goes beyond the scope of this study, see e.g., Roos et al,

Carbohydr. Res., 238, 398211;-48, 1993). In independent studies we have observed that different annealing rates typically lead to changes in T_g' of a few kelvins (D.A. Pedernera, PhD thesis, in preparation). The blue triangle in Fig. 6 was obtained by placing the measured T_g' onto the ice melting curve given by Koop et al., Nature 406, 611-614, 2000, assuming that hexagonal ice was formed (see also point 3). Hence, we believe that the blue triangle should remain in Figure 6.

8)

We replaced "agree nicely" by "are consistent with the data".

9)

We deleted the part as suggested by the referee.

10)

We include T_g^* for citric acid by Murray ACPD 2008 in our Fig. 7.

11)

Here, we disagree with the referee's statement: "... a glassy particle may not change composition with a change in humidity. Only increasing its temperature will allow it to take up water after passing over T_g ."

We are convinced that a glass transition can be induced by changing relative humidity, similar to the deliquescence process, where a crystalline solid transforms to a liquid by water uptake from the gas phase. For example, knowing the phase diagram (T vs. conc) of a water/solute system and the corresponding water activity in the liquid phase solutions it is straightforward to predict the deliquescence process and the deliquescence relative humidity (DRH) of the solute crystal in that system: Deliquescence occurs at the melting point curve of the solute crystal in the (T vs.

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conc) phase diagram. This curve is usually constructed from heating cycle melting point measurements, not by changing relative humidity. Nevertheless, when the water activities of the solutions are known, the DRH can be predicted and deliquescence does in fact occur precisely at that point, even if it is reached by changing relative humidity. Therefore, the corresponding state diagram containing the T_g curve (obtained from heating cycles) can be used to predict when the glass transition will occur upon changing relative humidity (when the water activities of the solutions are known). This is exactly what we have done. Diffusion in glassy particles is similarly slow as solid state diffusion in crystals. Nevertheless, deliquescence occurs as soon as the crystalline particle reaches its deliquescence relative humidity because water uptake starts from the surface of the particle leading to a liquid layer that propagates inward without the need for solid state diffusion. The same process is active in glassy particles when RH changes to a value above the glass transition curve (see also answer to referee 2). Note that because the glass transition is not a first order phase transition the liquefaction is not as sharp (i.e., more continuous) as that during deliquescence.

Therefore we add the following part as a footnote on page 9286 In 8 :

"The glass-to-liquid transition upon increasing RH is very similarly to a deliquescence process of a crystalline solid. The latter occurs as soon as the crystalline particle reaches its deliquescence relative humidity because water uptake starts from the surface of the particle leading to a liquid layer that propagates inward without the need for solid state diffusion. The same process is active in glassy particles when RH changes to a value above the glass transition curve."

12)
We do not claim that inorganic solutions do not form glasses at all. Based on our experiments and literature data we conclude that it is unlikely that either ammonium sulphate, sulfuric acid, nitric acid or ammonium bisulfate form glasses at atmospheric relevant temperature and relative humidity conditions (page 9290 In 1). With their experimental setup, Murray and Bertram, PCCP (2008) cannot observe glass formation

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and therefore, one does not know whether their solutions are highly viscous brines or whether they form glasses after ice formation. Furthermore, very recent preliminary experiments in our laboratory (unpublished) indicate that letovicite solutions between 40 and 55 wt% letovicite exhibit T_g values similar to those of sulfuric acid and ammonium bisulphate.

13)
The reviewer requests to remove the reference to RH and glass formation. We state in the manuscript on page 9291 ln4-6:

"Aerosol particles containing large and moderate hydrophobic organic molecules are most likely to form glasses at intermediate to high relative humidities in the atmosphere."

The answer to point 11 should clarify that we strongly believe that our statement regarding RH is valid which is why we decided to keep it in the manuscript. Note however, that we corrected the statement regarding the hydrophobicity issue (see point 6).

14)
We agree with the reviewer that we are a long way from understanding the role of glassy materials in the atmosphere, but modelling studies could improve our understanding substantially. Microphysical modeling, for example, could help to obtain a more quantitative assessment of the sensitivity of ice cloud formation on water uptake and diffusion in glassy particles. A global model scenario comparing aerosol populations that are either solely liquid/solid or also glassy could give a first estimate on how glassy particles could influence the radiative forcing. Similarly simple model runs were performed to investigate globally the influence of homogeneous versus heterogeneous ice nucleation (Zobrist et al. ACP 2006, Abbatt et al. Science 2006). Nevertheless, we reformulate the sentence starting with "We propose..." on page 9291

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In 17 to:

"In order to fully assess the influence of glassy aerosols on the direct and indirect aerosol effect on the local single cloud level as well as on the regional to global level, microphysical and/or large scale model studies are required to incorporate glass formation processes. Furthermore, our study shows that a better knowledge ..."

Technical issues

1)

We replaced "aerosols" by "aerosol".

2)

We generally broke down longer paragraphs into smaller ones.

3)

We replaced "quite" by "very" on page 9277 ln 22.

4)

We replaced the sentence on page 9295 ln 3-4 by "Thus the glass transition temperature can be calculated over the entire concentration range."

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 9263, 2008.

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