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Atmospheric Chemistry and Physics Discussions

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 anonymous referee #2 for his/her constructive comments. We have addressed the referee's concerns point-by-point below.

The reviewer's major concern is the fact that emulsions can not take up water during the experiments while aerosol can in the atmosphere.

First, we investigated also glass transitions in experiments in the absence of any oil matrix, which we termed bulk or large volume samples (in total, less than 20% of the glass temperatures are from emulsion experiments). The glass temperatures of such samples agree very well with those of the emulsified samples, as we stated on page 20 line 685/686:" No significant difference in the glass temperatures of an emulsion versus a bulk sample was observed." Furthermore, emulsions are more commonly used to investigate glass formation (e.g., Angell, Chem. Rev., 102, 26278211;-2649,

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2002), because this inhibits nucleation of ice or solute crystals thus allowing for the observation of a glass transition. Moreover, using the same type of experiments we have studied the homogeneous nucleation of ice in the past. Despite the fact that formally, the experimental trajectories differ from those in the atmosphere, we have applied these data with great success to the atmospheric situation (Koop et al., 406, 611–614, Nature, 2000). Here, we use the same principles to apply our data from the experiments to the atmospheric situation.

Considering aerosol particles in the atmosphere, it is very important to discriminate between water uptake in the glassy state and water uptake once RH has reached values above the glass curve. In the glassy state, water uptake is only possible by diffusion through the glassy matrix, which is slow and a process that is comparable to solid state diffusion. Only when the glass curve is crossed (i.e., at higher RH) a liquid layer forming at the surface can turn the whole particle into a liquid by shifting the glass phase boundary inward as outlined by the referee. Amorphous solid and the liquid coexist only during the actual glass transition process. This is very similar to the deliquescence behavior of crystalline aerosol particles, see also response to point 11 of referee 1.

The referee stated: "Probably there could be some suggestions on what experiments are needed to determine if glassy particles can form under atmospheric conditions as well as in emulsions."

Although we performed some experiments on small droplets embedded in an oil matrix, all investigated state diagrams have a clear atmospheric relevance. They show under which temperature and RH conditions typical aerosol constituents are expected to be glassy. The emulsion or bulk samples do not exhibit different glass formation abilities than atmospheric aerosols, since to our knowledge no dependence of the glass transition temperature on sample/droplet size is to be expected, different from homogeneous ice nucleation. This is, because the glass transition does not involve a nucleation pro-

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cess.

The goal of the present study was to introduce a novel microphysical process that has not been discussed so far for the atmospheric application and which might contribute to the supersaturation puzzle recently introduced by Peter et al., 314, 13998211;-1402, Science 2006. We hope that our study motivates other scientists to investigate whether the atmosphere provides the dynamic situations together with the chemical composition of aerosols that glasses might be indeed important. The latter point needs probably the deepest investigation. So far only a few studies (e.g., Murphy et al., J. Geophys. Res., 111, D23S32, doi:10.1029/2006JD007340, 2006.) provide some information on the chemical composition of the upper tropospheric aerosol.

Minor comments:

The water activity meter is specified in the Appendix A4 on page 22 line 767, but not in the main text on page 8 line 267. Therefore we replace "water activity meter" by "dew point water activity meter, see Appendix A4 for details" on page 8 line 267.

Concerning the difficulties with Fig.9. In the revised version, we labeled the x-axis with "time", without indicating a specific scale since it has only a qualitative meaning as it was stated correctly by the referee. We also changed the first sentence of figure caption 9 to: "Schemes for the physical states of model aerosols following the hypothetical trajectory shown in Fig. 8, starting from low to high RH and back to low RH."

The curve connecting the symbols in Fig.9 is not calculated but it is rather meant to act as a guideline for the aerosol path following the trajectory given in Figure 8. The relative humidity in Fig.9 reaches a maximum before the ice growth depletes the water in the gas phase, which is actually somewhere in between the two symbols above

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$RH(T_{\mathrm{hom}})$. But again, both axes have only qualitatively meaning.

Nitric acid as well as low molar mass organics can lower the glass temperature in mixtures but do not entirely stop glasses from forming. We try to treat this point while discussing aerosol composition in Chapter 6 and 7.

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

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