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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Heterogeneous freezing of single sulphuric acid solution droplets: laboratory experiments utilising an acoustic levitator" *by* M. Ettner et al.

M. Ettner et al.

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We thank the referees for their comments and remarks, which we want to discuss now and implement in the manuscript.

In general, the referees have many suggestions with respect to homogeneous freezing of solution droplets. Although we present homogeneous freezing data for comparision reasons, we want to focus the attention of the reader on heterogeneous nucleation. An article focusing on homogeneous ice nucleation investigating H2SO4/HNO3/H2O-solution droplets will appear soon. An extensive set of data on homogeneous ice nucleation will be presented there.

Referee#1:

1+2: The large scatter of the homogeneous freezing temperatures in figure 6 and in figure 7 are the result of contamination problems, which we have with the current experimental setup. For that reason, we will present in a revised form of the article only those points, which reached the lowest freezing temperatures in a concentration range. These droplets can then be considered to have frozen homogeneously.

For comparison, we include the parameterization for homogeneous nucleation temperatures of aqueous solutions [Koop et al., 2000] in the figures. The nucleation rates were assumed to lie in the range 1-100 cm-3s-1, which, considering the observed freezing times, is applicable to our drop experiment.

The paper has been correspondingly modified to reflect these changes.

3: The evaporation of H2O does lead to a cooling of the droplets, especially during the first few minutes of the experiment. However, the volume decrease slows down with time, as shown in figure 5a. At the moment of freezing, the rate of evaporation is extremely low and evaporative cooling can be neglected. .

4: The heating of the droplet due to the ultrasonic field was measured by means of a thermocouple. We placed a droplet at the tip of the thermocouple and positioned it in the ultrasonic field. This measured temperature was always approximately 2°C higher than the temperature measured with the Pt-100 sensor, which was positioned next to the droplet for the whole range of temperatures. The Pt-100 sensor was the sensor we used during our real experiment, and we concluded that the ŞrealŤ droplet temperature is the Pt-100 value corrected by 2°C.

5: In the context of aircraft emissions soot particles can be covered by sulfuric acid and/or polycyclical organic compounds resulting from the combustion. This is detailed for example in the IPCC report "Aviation and the global atmosphere", 1999. The emitted soot particles are agglomerates of up to several hundreds of small, primary graphite spheres with size diameters roughly between 10 and 50 nm. The structure of these primary particles has been shown to be graphitic [Charlson and Ogren; Burtscher; La-

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haye]. Since the droplets investigated upon in this paper are binary sulfuric acid water solutions the possible cover of the soot particles with H2SO4 probably does not play a role for the heterogeneous freezing. Only the polycyclical organics present at the surface of the soot particles may influence the freezing. In this respect our experiments are incomplete and future experiments should be performed with combustion generated soot particles. Here too caveats exist because the nature of the combustion process itself influences the properties of the resulting soot particles. In this respect our experiments show that plain soot graphite already influences the heterogeneous freezing. Whether the presence of organics further enhances (or suppresses) this influence is left open here. Probably the organic coating is removed when the particles is immersed in a solution increasing the likelihood of heterogeneous freezing because experiments by Diehl et al., 1998 with a kerosene-burner showed that the resulting soot particles are poor contact nuclei (while they are coated with organics) but good immersion nuclei.

6: This is a valid point and further experiments reducing (or at least assessing) the number of soot or graphite particles injected into the sulfuric acid solution droplets are being designed. In the aircraft exhaust primary soot particle number densities are quite high, because for the onset of their agglomeration values up to 1012 per cm3 of air are necessary [Petzold, 1995]. Therefore in the process of droplet formation and heterogeneous freezing soot/graphite particle numbers higher than 1 per droplet may be involved. Based on our experiments we merely conjecture that the emission of soot by aircraft may influence the freezing of cloud solution droplets. Whether this effect is significant in an atmospheric context needs to be addressed by further laboratory experiments as well as field studies.

Referee#2:

Comparison:

For homogeneous nucleation:

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For comparison, we include the parameterization for homogeneous nucleation temperatures of aqueous solutions [Koop et al., 2000] in the figures. The nucleation rates were assumed to lie in the range 1-100 cm-3s-1, which, considering the observed freezing times, is applicable to our drop experiment.

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For heterogenous nucleation:

We have reacted to the suggestion to compare data from other heterogeneous experiments by including the fit curve to the heterogeneous freezing study by Zuberi et al., 2002 in our figure7. In this study heterogeneous freezing of (NH4)2SO4 droplets loaded with kaolinite and montmorillonite (k-10 with enhanced surface area) particles were investigated. We cannot directly compare this results with ours, because we have a different droplet composition, but in general our heterogenous freezing temperatures are about 10°C higher than those found by Zuberi et al. This can be accounted for by considering the differences in drop volumes between those used in the experiments cited and the ones used in the present study. An interesting observation is that Zuberi et al. made one common fit for heterogeneous freezing induced by both kaolinte and montmorillonite (k-10). We also found that the heterogeneous nucleation temperatures for these two materials are quite similar. In contrast using another variety of montmorillonite (KSF), which was not processed for surface enhancement, we found still higher heterogeneous freezing temperatures. Most likely this efficient heterogeneous nucleation at higher temperatures is due to the fact that the montmorillonite (KSF) particles are larger and thereby posess more active sites.

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Freezing at the surface: The particles are continuously moving due to the internal circulation of the droplets. That means they are moving in and out of the surface. In the case of graphite particles most particles seem to be on the surface after freezing, because the graphite particles show up prominently against the ice backround. For other substances the contrast between the particle and the ice backround is not so high.

Referee#3:

Comparision:

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It was pointed out, that the freezing temperatures for homogeneous freezing presented in this paper, are higher compared to the results found by other authors. The higher freezing temperatures are expected, because the size of the investigated droplets differ from the size of droplets analysed by these authors (Bertram 1996, Koop 1998, Vortisch 2000).

For example for pure water, the volume difference between a 1mm-diameter droplet and a 10μm droplet produces approximately 4°C difference in the freezing temperatures for a cooling rate of approximately 1°C/min. (Pruppacher, Klett, 1997)

Properties of the used substances: We used the commercially available substances graphite, kaolin, montmorillonite (K-10) and montmorillonite (KSF) as heterogeneous freezing nuclei. The size of the particles were as follows: graphite 1-2μm, kaolin 3-4 μm, montmorillonite (K-10) 3-4 μm and montmorillonite (KSF) 20-25 μm. According to the manufacturer, the surface area of montmorillonite (KSF) is 20-40 m^2/g, whereas the surface area of montmorillonite (K-10) is 220-270 m^2/g. The larger size of the montmorillonite (KSF) particles and thereby a higher probability of possesing active sites is most likely responsible for the relatively higher nucleation temperatures as compared to that of montmorillonite (K10).

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 1887, 2004.