

## ***Interactive comment on “Inhibition of ice crystallisation in highly viscous aqueous organic acid droplets” by B. J. Murray***

**B. J. Murray**

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The author thanks referee 2 for her/his helpful comments.

The referee's comments are italicised and the author's response is in normal type.

*p. 8750: If the very concentrated droplets did not nucleate ice on warming (line 18), then the melting point means something different because the phase that is melting would have a different energy than the crystalline phase. Is there any information about the glassy phase that can be obtained from the lack of a big offset in the melting point curve for the solutions that never nucleated ice?*

Ice melting was not observed for very concentrated droplets (59.6 and 61.2 wt%) since no ice crystallised. The droplets remain liquid on cooling, forming a glassy solid and then on warming devitrify to form a liquid. No crystalline solids formed in these droplets

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and the ice-liquid equilibrium line (solid black line) represents the temperature below which the liquid becomes metastable with respect to ice. This section seems to have caused some confusion and it has been rewritten and now reads as follows:

'Freezing temperatures have been recorded for droplets with concentrations up to 49.2 wt%. Insufficient ice crystallised in droplets of higher concentration to identify a freezing temperature (the technique for measuring crystallisation temperatures with XRD is sensitive to 10 wt% of the overall mass of the droplets changing phase). Ice crystallisation was not observed in droplets of >49.2 wt% on cooling, but in some cases ice crystal growth was detected at ( $T_w =$ )  $211 \pm 6$  K as the droplets were warmed at 5 K min<sup>-1</sup>.  $T_w$  was measured between 49.2 and 54.4 wt%. For concentrations between 54.4 and 58.2 wt%  $T_w$  was not determined, however ice did crystallise on warming at some temperature below the ice-liquid equilibrium curve and  $T_m$  could then be determined. The fact that ice crystallised on warming droplets of between 49.2 and 58.2 wt% indicates that nucleation of ice took place at some lower temperature, but crystal growth rates only became comparable to the warming rate at around 211 K or above.

Droplets with concentrations of 59.6 and 61.2 wt% did not crystallise on cooling to 173 K or on subsequent warming indicating that nucleation of ice did not occur at all in these very concentrated solution droplets. These droplets most likely formed a glassy solid before they became sufficiently supersaturated for nucleation, hence nucleation was inhibited and they therefore did not crystallise on cooling or warming. This will be discussed in more detail in section 3.3.'

*p. 8750: When the emulsion droplets froze on warming, did they freeze to cubic or hexagonal ice?*

Preliminary experiments indicate that the phase that crystallises on warming is cubic ice. The current experiments were not designed to routinely determine the phase that crystallised on warming, only if ice crystallised.

*pp. 8756-8757: When the manuscript discusses the differences between particles in*

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*an emulsion and in the atmosphere, mass transfer is mentioned: unlike droplets in an emulsion an atmospheric particle can take up water and be diluted. There are also differences in heat transfer between particles in an emulsion and the atmosphere that should be mentioned. Probably these heat transfer differences are small in the absence of latent heat release, but they might change the way crystallisation on warming occurs.*

The topic of heating during crystallisation has been addressed in the past [Murray and Bertram, PCCP, 2006; Murray et al, Nature, 2005]. Heat release and droplet warming is an issue in pure water droplets or dilute solutions where crystallisation is fast in comparison to heat dissipation; however it is shown that it is slow in concentrated solution droplets and the experimental results are therefore relevant for the atmosphere. In order to address this point the following has been added to the experimental section:

'The rate of transfer of heat evolved during crystallisation to a droplet's surroundings should be considered when interpreting data from emulsified samples. Heat transfer calculations (see Murray and Bertram, 2006 and Murray et al., 2005) show that when crystal growth is rapid, such as in pure water, droplets will heat up more when suspended in gas than if in an oil matrix. Whereas ice crystallisation and corresponding heat release in micrometer sized concentrated solution droplets (in which ice Ic forms) is slow relative to heat dissipation in either oil or gas and these droplets do not heat up significantly. Hence, the results presented here for concentrated solution droplets, where crystallisation is relatively slow, are directly relevant to the atmosphere.'

*p. 8757: Kärcher and Koop (2005) considered not only a lower condensation coefficient of water on organic solutions but also insoluble organics that would have less water uptake at equilibrium.*

The pertinent paragraph has been modified, it now reads:

'In a modelling study, Kärcher and Koop (Kärcher and Koop, 2005) suggested reduced water uptake into organic aerosol might explain this observation. Reduced water uptake might be caused by a smaller accommodation coefficient or a lower water content

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at equilibrium relative to inorganic aerosol resulting in smaller droplets which are less likely to freeze.'

*Zobrist, B., C. Marcolli, D. A. Pedernera, and T. Koop, Do atmospheric aerosols form glasses? Atmos. Chem. Phys. Discuss., i, 9263-9321, 2008.*

Corrected

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 8743, 2008.

**ACPD**

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