Response to anonymous referee #2

The referee's comments are italicized and our responses are in plain text

The authors report about laboratory experiments on ice nucleation of single droplets, exhibiting liquid-liquid phase separation. Experiments on droplets using a Raman microscope have been performed on similar systems before, but the authors extend those measurements to lower temperatures and use a clever experimental approach to distinguish different mechanisms of heterogeneous ice nucleation in phase separated organic-inorganic mixtures. Besides showing that depending on the phase state of the organic phase, nucleation occurs either at the ammonium sulfate core or on the organic surface of these particles, they also show that phase separation has only a minor effect, if any, for deliquescence and efflorescence of ammonium sulfate over the whole temperature range encountered in the atmosphere.

The authors would first like to thank anonymous referee #2 for their insightful comments that have improved the clarity of this manuscript.

page 30954, lines 17-22: The statement that mixed organic-sulfate particles always exhibit a fully engulfed core-shell morphology is not true in general. As pointed out by e.g. Kwamena et al. (2010) this depends on the relative magnitudes of the different surface/interfacial tensions. For example Song et al. (2012) showed that their C6/AS/H2O mixture (C6 being a mixture of three C6 dicarboxylic acids) exhibits partially engulfing. Please reformulate your statement. Also, I wonder if the conclusion of your experiments does not imply that even a partially engulfed particle at low temperatures would nucleate at similar supersaturations, since it seems not to matter so much whether nucleation occurs at the surface of a semisolid organic or the AS core?

The authors thank referee #2 for catching this oversight—this sentence now reads "Partial engulfment has also been shown for mixed organic-sulfate particles that have undergone LLPS and subsequently effloresce (Song et al., 2012). However, it has been shown from 2D projections that many phase-separated, effloresced organic-sulfate systems assume a fully engulfed core-shell morphology, with an evenly thick organic coating and a crystalline ammonium sulfate core (Ciobanu et al., 2009; Bertram et al., 2011; Song et al., 2012)."

While the authors agree that an interesting interpretation of the results of this manuscript may be that partially engulfed particles would nucleated ice at similar supersautrations as fully engulfed particles, since it seems to not matter so much whether nucleation occurs at the surface of a semi-solid organic or the AS core, we are unable to add any conclusions to this manuscript about partially engulfed particles since they were not observed or studied in this work.

page 30961, line 2: compare with the estimate in Ciobanu et al. (2010). This seems very fast to me, also the diffusion constant will change drastically with temperature (long before becoming glassy).

The authors have added the estimate found in Ciobanu et al. (2010) as well as an estimate of the timescales for diffusion through a 1 μm organic shell. This sentence now reads: "The diffusion coefficients for a small molecule like water diffusing through a liquid organic matrix is ~10^{-5} to 10^{-7} cm^2 s^{-1} (Ciobanu et al., 2010; Shiraiwa et al., 2011). Thus, a small molecule like water should be able to diffuse through a 1 μm liquid organic coating on the order of microseconds to milliseconds."

The authors also acknowledge that the diffusion constant will change with decreasing temperature; however, a recent parameterization from Zobrist et al. (2011) suggests that the diffusion constant of water through sucrose stable liquids minimally varies over the temperature range probed in this study.

page 30968, line 9: the data point at 210 K lays significantly above the homogeneous freezing line, as you also point out. What do you think is the reason for the deviation: Could it be that your calculated Scrit is too high below 215 K? Or do you believe that this is an indication for the Koop line being wrong below 215 K? Since also the 210 K points in Fig. 9 are higher than immediately obvious (I cannot see a reason for the apparent increase in Scrit from 215 K to 210 K in Fig. 9); I tend to believe in a problem of the setup at these very low temperatures. Please comment.

With our experimental setup, there are two possible factors that could lead to an overestimation of S_{crit} at low temperatures. The first is the slow growth of ice to a visually detectable size. The authors do not believe this is a problem for the homogeneous freezing of these nebulized droplets because the initial particles are large and the resultant ice particle grows quickly due to the water already present in the particle. The second reason could be our temperature calibration. As explained in the Section 2.1, the lowest point in our temperature calibration is the ferroelectric phase transition of ammonium sulfate at 223.1 K. Thus, we are slightly outside of our calibration curve at these low temperatures and cannot exclude this factor. Despite the possible effect of this factor, the authors believe that these homogeneous freezing points are real. Similar results at low temperature have been observed in a different experimental setup, the AIDA chamber, for homogeneous freezing of sulfuric acid particles (Mohler et al., 2003). Here, the slope of the homogeneous freezing curve is slightly altered from the Koop homogenous freezing line. These results have also been seen for homogeneous freezing of organic particles using the AIDA chamber (Wilson et al., 2012). This slightly altered slope is qualitatively similar to the slope of our homogeneous nucleation data; however a more in depth analysis of the meaning behind this slightly altered slope is beyond the scope of this manuscript.

In light of the referee's comment, the following sentences have been added to section 3.3: "It should be noted that the slope of our homogeneous nucleation points is slightly skewed from the line of Koop et al. (2000) for a homogenous nucleation rate of $5x10^9$ cm^{-3} s^{-1}. This could be the result of our lowest temperature points being slightly outside of our temperature calibration curve as the lowest point in our calibration curve is the ferroelectric phase transition of ammonium sulfate at 223.1 K; however, groups studying the homogeneous nucleation of sulfuric acid (Mohler et al., 2003) and organics (Wilson et al., 2012) using the AIDA chamber have observed slopes similar to ours.”

page 30965, line 14-22: this is very speculative and cannot inferred directly from the experiments. I feel the speculative character of this paragraph should be pointed out more clearly.

We have added a comment that emphasizes that this is a speculative comment made without any hard experimental evidence. The sentence now reads “Although we are unable to probe this effect with our current experimental setup, we attribute this ice nucleation efficacy to the incorporation of water molecules into the glassy matrix.”

page 30967, line 1-4: your experiments indicated that the critical diffusion time for the particles of the size in your setup is reached between 220 K and 215 K. You could apply eq. (1) to give a rough estimate of the relevant viscosities.

These calculations have been added to the manuscript in section 3.4.

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