

## **Response to Anonymous Referee #2**

We appreciate the comments of Referee #2, which we have repeated in italics below. Our responses follow the comments. Several important issues were raised that suggest the manuscript was not sufficiently clear. We have addressed these issues in our responses:

*1. There are several possible caveats regarding the experimental and modeling methods, which should be addressed, including:*

*a) It is unclear to me, how droplet position was converted to droplet residence time. It seems that the radial velocity (and temperature) distribution of the laminar flow was not taken into account.*

We have shown in [A. F. Khalizov, M. E. Earle, W. Johnson, G. D. Stubbley and J. J. Sloan, “Development and Characterization of a Laminar Aerosol Flow Tube,” Review of Scientific Instruments, 77(3), 2006] that both radial velocity and radial temperature gradients in the flow tube are negligible as a result of the flow tube design. To be certain that any small residual gradients are accounted for in the present experiments, we used cross-sectional- and mass-averaged temperature profiles determined from Computational Fluid Dynamics (CFD) simulations. These profiles incorporate the radial distributions of gas flow velocity and temperature, so the correct droplet residence time at any axial location can be determined simply from the total flow rate. This aspect of our experiment

is described in Sect. 2.4 of the manuscript, and in greater detail in our previous work, which we have cited above.

*b) As freezing is strongly nonlinear with temperature, even small temperature variations may dominate the ice signal. In Fig. 7, the temperature has a minimum around  $t=10s$  which is almost 1K below the temperature at 23s. Where does this minimum come from? How does the temperature profile depend on the radial position?*

The slight minimum in the temperature profile around  $t = 10$  s in Fig. 7 results from the way the axial temperature profile was achieved. The axial profile is determined by a combination of two effects: the location of the slightly warmer (conditioning) section above the test section (Section C) and the fact that the nitrogen coolant flows from top-to-bottom through two interwoven copper cooling coils on each section wall which causes the upper part of the test section to be slightly colder than the lower part. After extensive tests, we concluded that this configuration causes the smoothest axial temperature gradients in the gas. It achieves the desired (rapid, smooth) cooling, because the warmer gas from the upper conditioning section is first exposed to a slightly lower temperature at the top of section C, which cools it rapidly to the desired experimental temperature, which is that of the lower part of the section. The balance between the need for rapid cooling and the need to stabilize the gas at the required temperature results in the slight minimum in the axial temperature profile noted by the referee. Regarding the radial temperature distribution – the uniform wall cooling and the presence of crossed, cooled fins along the centre axis of the flow tube, reduces the radial temperature gradient to a

negligibly small value. This was confirmed by both our CFD simulations and measurements with thermocouples distributed across the radius during the characterization of the tube. As a final precaution, however, we used cross-sectional- and mass-averaged temperature profiles, as explained above, to account for any small gradients that might have remained.

*c) There seems to be substantial evaporative cooling of the liquid droplets as soon as the first ice is formed. This should be included in the process model, as even small temperature fluctuations can have a large effect.*

The evaporative cooling of liquid droplets when ice is formed was discussed previously in Short Comment C8075; here we summarize the important parts of this discussion. In a typical experiment, only a small fraction (less than 5%) of the droplets nucleate and freeze, so there are significantly more droplets than ice particles. The experiment is designed so that the droplets are in thermal equilibrium with the surrounding gas and also in chemical equilibrium (*i.e.* the chemical potentials of the water in the gas and droplet phase are also as close to equal as possible). The ice particles are in thermal, but not chemical equilibrium with the gas. As a result, the deposition rate on the ice particles far exceeds the evaporation rate from the large number of droplets, and the droplet temperatures are not affected by evaporation. At lower temperatures, the fraction of droplets frozen increases; but because the partial pressure of water vapour is correspondingly lower, the evaporation rate and hence the droplet cooling are both very small in this case as well. This suggests, however, that we should consider the possibility

that the rapid deposition of vapour may warm the ice particles relative to the surrounding gas, which might change the vapour uptake rate. To investigate the possible consequences of this eventuality, we carried out a series of model sensitivity tests. We found that temperature increases of up to 0.3 K did not significantly influence the mass accommodation coefficients reported in the manuscript (see Short Comment C8075 for details). We note also that the same 0.3 K temperature increase changed the nucleation rate coefficients by less than 4%.

*2. There are several features in the experimental results that indicate problems with the data evaluation:*

*a) In Fig. 4, water and ice seem to coexist over a temperature range of almost 5K. This is much too large for any reasonable parameterization of homogeneous freezing.*

This is not a water-ice equilibrium situation. The coexistence of water and ice illustrated in Fig. 4 reflects both the probabilistic nature of the nucleation process and the short timescale (about 35 s) of the freezing experiments. Moreover, as detailed in Sect. 4.3 of the manuscript, the evolution of this mixed-phase aerosol as a function of temperature establishes the kinetic timescale over which nucleation occurred, which provides the basis for our determination of freezing rates and mass accommodation coefficients.

*b) In Fig. 5, small and medium sized droplets freeze more readily than large droplets. This is opposite to what is expected from homogeneous nucleation. Large droplets should*

*freeze first, small droplets last upon cooling. Apart from the shift, the shape of the respective curves should be the same however.*

The reviewer is correct that, according to homogeneous nucleation theory, large droplets should freeze more readily than small and medium sized droplets. This is indeed seen to be the case if one calculates the total nucleation rate in  $\text{s}^{-1}$  from  $J_V(T)V$  at a given temperature, using the  $J_V$  values for the different sizes in Fig. 12 and the volume  $V$  computed from the corresponding mode radii. This calculation yields a rate which increases with droplet size. For example, at 235.4 K, the total nucleation rates are  $1.0 \times 10^{-2} \text{ s}^{-1}$ ,  $3.5 \times 10^{-3} \text{ s}^{-1}$ , and  $9.3 \times 10^{-4} \text{ s}^{-1}$  for large, medium, and small particles, respectively. The freezing curves in Fig. 5, however, show the temperature dependence of the volume fraction of ice, which depends on the rates of both nucleation and mass transfer to the nascent ice crystals. The shift of the freezing curve of the large droplets to lower temperatures (and the corresponding change in the shape of the curve) in comparison to the curves for small and medium particles results from the combination of these two processes and is not a violation of homogeneous nucleation theory. In Sect. 2.4 of the manuscript, we discuss the use of freezing curves to determine nucleation temperatures and we note that these data cannot be used to determine nucleation rates because of the complicating influence of mass transfer. This limitation provides the motivation for using the microphysics model, which includes both of these processes.

*c) What is the origin of the minimum in Fig. 7, upper panel? As can be seen in Fig. 10, the fits converge to completely unphysical slopes of  $\ln J(T)$  (parameter  $a_v$  in Eq. 17), if*

*applied to a single temperature. The individual points are off by up to almost one order of magnitude from the group fit and no difference was found in  $J(T)$  for the two warmest temperatures.*

The minimum in the axial temperature profile results from the cooling configuration of the experimental apparatus, as discussed above in response to comment 1(c). It is true that the  $J_V(T)$  curves from fits to single experiments in Fig. 10 depend strongly upon temperature and therefore they are very sensitive to the axial temperature profiles. By performing model fits for groups of experiments (group fits), we not only determine a single  $J_V(T)$  curve applicable over a broader temperature range, but also mitigate the effect of the strong temperature dependence of individual experiments. This is an important point, and so we have added it to the discussion in Sect. 4.3 of the manuscript so that it will be clear to the reader.

*3. Despite these problematic findings, no error bars were given in Fig. 12 for the results obtained. Rather strong conclusions with respect to a possible contribution of surface nucleation were drawn especially in the follow up manuscript.*

We agree that the uncertainties are very important. Following the discussion in the response to comment 2(c) above, we determined the limits of uncertainty for the group fits for each droplet size. Our response to Referee #1 gives the details of the approach we used for this and includes a new figure that shows the resulting temperature-dependent uncertainties for the  $J_V(T)$  curves. Briefly, these were obtained by repeating the group fits

for each droplet size  $N$  times and removing one of the  $N$  individual freezing experiments in each successive run. The standard deviations of the resulting  $J_V(T)$  curves were used to determine the uncertainties for the results with each droplet size. Based on these uncertainty limits, it can be concluded that the size-dependent differences we report are indeed significant; *i.e.* they remain when the uncertainty of the group fits is taken into account. Since the observed differences with droplet radius are significant, we conclude that a contribution from surface nucleation can be determined from our data. This aspect is treated in the follow-up manuscript.