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Interactive comment on "Experimental investigation of homogeneous freezing of sulphuric acid particles in the aerosol chamber AIDA" *by* O.Möhler et al.

O.Möhler et al.

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Reply to Referee #1 and Referee #2

First of all, we would like to thank both reviewers for their general and specific comments on our paper. Here we address the specific points and questions of both reviewers and will also refer to some points made by the reviewers of the companion paper (Haag et al.) as far as the experimental methods are concerned.

Minor Comments by Referee #1:

Page 1440, line 3-4: Concerning the agreement between Lyman alpha and chilled mirror hygrometer data, we change the text as follows: "Water vapour mixing ratio (panel c in Fig. 6) is measured with the fast in situ Lyman-α hygrometer (FISH) of

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Forschungszentrum Jülich (Zöger et al., 1999) which is, however, run as an ex situ instrument during the AIDA experiments (Fig. 1). The FISH was calibrated against a high precision frost point hygrometer (MBW DP30). Under constant p,T-conditions in the aerosol chamber the calibrated FISH agreed well with another commercial chilled mirror hygrometer from General Eastern (type 1311 DR-XP) which was used to measure water vapour in the aerosol chamber. This instrument was, however, sensitive to sulphuric acid aerosol deposition on the frost point mirror, which had to be cleaned at regular intervals, and provided only limited information during dynamic expansions because its response time on changing pressure and humidity conditions is too long."

Page 1441, lines 10-20 will be changed as suggested by the reviewer.

Page 1443, line 7 will be changed as suggested: "...evaporate at S_{ice} less than 1."

Page 1450, line 19-20 will be changed as suggested: "...difference between the activity of water in the supercooled droplets and in a solution in equilibrium with ice at the same temperature (Koop et al., 2000)."

FTIR spectra showing ice particle formation were measured during the most recent experiment series at a rate of 3 spectra/min, which is not sufficient for the purpose of this paper. Therefore the FTIR results will be discussed in a separate paper.

Major points made by Referee #2:

The reviewer made a good point about the steeper slope of data from series A in Fig. 7 and especially about the low S_{nuc} measured during experiments A6_1 and A6_2. Note, however, that at least part of the apparently steeper slope is due to the size and temperature dependent non-equilibrium composition of the aerosol particles which affects the nucleation rate and therefore the onset relative humidity (see also discussion of critical nucleation rates in section 4.2). At the lowest temperatures, for instance, ice nucleation occurs in significantly smaller particles and therefore at higher relative humidity with respect to ice (RHi), because larger particles are not in thermodynamic

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equilibrium due to decreasing water condensation rate (here we also refer to the companion paper and the authors' comment about minor point (14) of referee #1). The aerosol composition during volume expansions could not accurately be measured with the ACMS because of the relatively slow response time of the instrument to changing sulphuric acid concentrations. The aerosol water content $q_{ae,nuc}$ given in Table 1 refers to the thermodynamic equilibrium composition.

Experiments A6_1 and A6_2 are the only ones that disagree, beyond error bars, with the other data sets and with the water activity based parameterisation. We have carefully reanalysed experiments A6_1 and A6_2 which where exceptional in several respects: They were the very first experiments with an usually high concentration of background particles forming upon addition of synthetic air to the cold evacuated chamber (another gas supply system was used in later experiments to minimise that effect). While RHi over ice-covered walls at constant pressure and temperature before expansion was normally in the range $90-95$ % (due to a small difference between T_{wall} and T_{gas}), it appeared to be as low as 83 % in experiments A6_1 and A6_2 according to the FISH. We now recognised that the water mixing ratio $q_{g,nuc}$ of about $200\ ppm$ in experiments A6_1 and A6_2 was by far the highest in the whole set of experiments (see Table 1). During experiment series A, when the FISH instrument was run for the first time at the AIDA chamber, the water calibration had been limited to the linear range 5 - $100\ ppmv$ for technical reasons. Measurements of larger water vapour mixing ratios were evaluated assuming constant linearity. Recent work showed that the calibration curve is not exactly linear to high mixing ratios. Taking this into account yields an ice saturation ratio of 1.4 ± 0.11 for freezing onset of experiments A6_1 and A6_2 (instead of 1.29 ± 0.08). The same correction shifts the initial RHi before pumping from 83 % to a more reasonable value of 93 %, in agreement with the chilled mirror that measured (90 ± 9) %. Now, the data agree with those of series B within experimental uncertainty. The higher relative humidity also lowers the calculated equilibrium sulphuric acid concentration $w_{SA,nuc}$ to about $22\ wt.\%$. All other data in Figure 7 are not affected by the new evaluation of the FISH calibration.

Concerning referee's remark about heterogeneous nucleation on background aerosol: Each series of experiments in Table 1 is ordered by increasing temperature T_0, i.e. *not* in temporal order.

We will make the following changes in the manuscript:

Table 1 and *Figure 7* will be corrected for the new results as discussed above. Individual error bars including the errors of gas temperature, water vapour from the FISH measurements, and freezing onset time have been added to Figure 7. The errors will also be specified in Table 1.

Page 1435, line 7: "...the ice coating estabishes a relative humidity RHi with respect to ice between 90 and 95 $\%$ because T_g is slightly higher than T_w due to heat sources in the chamber (e.g. heated sampling tubes for water measurements).

Page 1441, line 26-28: We drop the sentence "Considering the uncertainties of T_g and q_t as discussed above, the uncertainty of the ice saturation ratio S_{nuc} calculated at t_{nuc} is about ± 0.05 at 230 K and ± 0.12 at 190 K". The discussion of uncertainties in S_{nuc} is delayed to *page 1447, line 13*, where we make the following change: "Uncertainties of S_{nuc} are calculated from the uncertainties of $T_{g,nuc}$ (± 0.3 K), q_{nuc} (± 6 $\%$), and t_{nuc} (see Table 1). The largest contribution is due to the uncertainty in $T_{g,nuc}$ because $(\partial lnS/\partial T)_p = \Delta H/(RT^2)$ shows a square dependence on temperature ($\Delta H =$ enthalpy of sublimation of ice, taken from Marti and Mauersberger (1993)). For experiments A6_1 and A6_2, a somewhat larger statistical error of ± 10 $\%$ was estimated for q_{nuc} because the FISH had been calibrated in the range 5 to 100 ppm, and this calibration curve had to be extrapolated to determine exceptionally large mixing ratios of about 200 ppm in these experiments."

Page 1447, line 27 to page 1448, line 1 will be changed as follows: "The data points of series A follow a steeper slope compared to series B. At least part of the steeper slope is due to the size and temperature dependent non-equilibrium effects discussed above and in the companion paper. At the highest temperature in series A (experiments A6_1

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and A6_2) the freezing onset occurred at a lower saturation ratio compared to the later experiment series B. Because the background aerosol concentration was unusually high during these experiments (about $10\ cm^{-3}$ even after pumping off to 10 hPa and refilling with synthetic air), it cannot be totally ruled out that freezing was affected by heterogeneous nucleation”.

Minor technical comments of Referee #2

Page 1430, line 21: Following the suggestion of the refree we write ”Homogeneous freezing nucleation in . . . ”

Page 1431, line 13-16: To avoid misunderstanding we write ”In the arctic stratosphere, formation of solid PSC particles is thought to be mainly initiated by homogeneous ice nucleation in supercooled ternary solution (STS) droplets which can be formed by uptake of water and nitric acid vapours into sulphuric acid particles at high cooling rates (Carslaw et al., 1997).”

Page 1432, line 20: o.k.

Page 1432, line 24: ”Number densities of aerosol particles exceeded typical atmospheric concentrations which, however, doesn’t affect the applicability of the present study to atmospheric conditions”

Page 1433, line 16: o.k.

Page 1440, line 5: Yes

Page 1440, line 12: ”This refers to a typical pressure of about 60 to 70 hPa in the measuring cell. The corresponding detection limits for water vapour in the aerosol chamber are about 0.004 Pa at 180 hPa total pressure and 0.02 Pa at 1000 hPa total pressure.”

Page 1443, line 9-15: To explain this we add to line 15: ”The second rise in the depolarisation signal is due to the subsequent ice crsytal growth as water vapour is replenished

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by evaporation from the ice-coated chamber walls."

Page 1444, line 2: o.k.

Page 1445, line 19-23: When cooling starts the particles become more dilute by taking up water from the gas phase. At the same time the sampling efficiency of the aerodynamic lens system changes and the particle number density decreases while the chamber pressure drops. These effects nearly compensate each other until the first large ice crystals are detected. Note that the integrated area under the ice particle spikes is small compared to the background signal.

Page 1445, line 23: Errors will be added to Table 2

Page 1447, line 15: o.k.

Page 1447, line 15: Yes, this was a typo.

Page 1450, lines 6, 13, 19: o.k.

Page 1456, Table 1: The cooling rate $\gamma_{nuc} = (dT/dt)_{nuc}$ is already listed in the table.

Referring to the Referee comments of the companion paper:

Referee #1, Point (11):

To discuss the possibility of adiabatic temperature control by wall cooling we add the following paragraph to page 1441, line 9: In previous cloud chamber studies this wall effect was minimised by controlled lowering of the wall temperature during pumping (DeMott et al., 1990). This technique could not be applied in our experiments because the AIDA chamber has a surface area of ca. $100\ m^2$. Controlled and homogeneous cooling of such a large area is not possible at the required rate.

Referee #2 (optical particle counter):

The discussion of the optical particle counter measurements will be revised by adding the following sentence on page 1444, line 5 after "between 0.1 (B4_1) and 25 % (A3_2)":

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”The increase of the ice particle number count may be delayed due to partial evaporation of ice crystals in the slightly warmer sampling tube. Furthermore, the sampling efficiency is less than $100\ \%$ for particles with mean diameters larger than about $10\ \mu m$ (Davies, 1968).

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