Anonymous Referee #3

Referee comment on "High Homogeneous Freezing Onsets of Sulfuric Acid Aerosol at Cirrus Temperatures" by Julia Schneider et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-319-RC3, 2021

We thank referee #3 for his or her thoughtful and detailed comments and feedback. Please find below our responses and suggestions for the manuscript revision, with the referee comments in black, our answers in green, and suggested changes or additions to the manuscript in blue.

In this work the authors investigate the homogenous ice nucleation of aqueous solution droplets in a cloud chamber. The authors carry out a literature review on the freezing thresholds reported for sulfuric acid solutions. They also collect results from prior experiments and perform new ones using the same experimental setup. Their experiments show that at low temperatures there are large deviations in the measured homogeneous freezing thresholds, when compared against a widely used parameterization. Based on this they propose a new parameterization to be used in atmospheric models. Homogeneous ice nucleation is still far from being completely understood, especially at low temperature where it can impact the formation of polar cirrus. This work is relevant to the scientific community. The experiments use established techniques and present interesting results. On the other hand, the analysis of the results is overly simplistic omitting several important factors. The usefulness of the derived parameterization is not clear. These issues should be addressed before the work could be suitable for publication in ACP.

General Comments:

Two other reviewers have already made comprehensive comments pointing out some of the major issues of the paper. Hence, I would emphasize some points that may require further discussion.

- The authors should include their data points in Figure 1 with their estimates of aw, or if it turns out too busy, make a separate figure depicting Tf vs aw. This would allow an easier comparison against the Koop et al (2000) results.

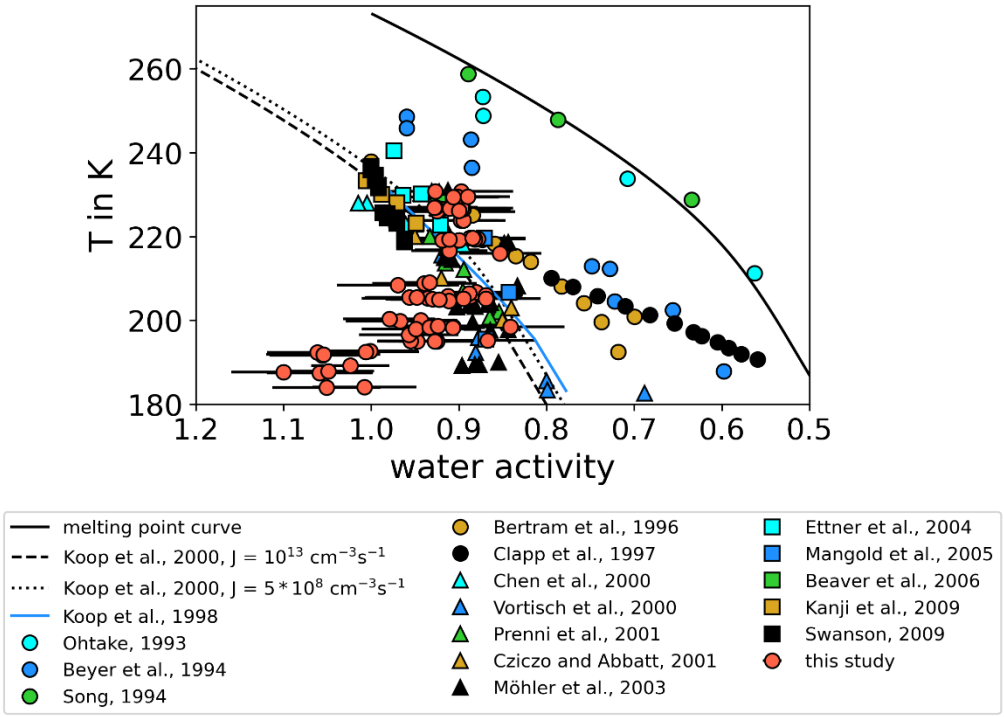

Fig. 1: Water activities of the AIDA results of this study in comparison to the summary of homogeneous freezing experiments shown in Fig. 1 in the manuscript.

This is a good suggestion. In the above Fig. 1, we added the AIDA sulfuric acid data to Fig. 1 of the manuscript. For the calculation of a_w, we assumed equilibrium conditions and therefore $a_w = RH_w$. The ice onset ice saturation ratios S_{ice} were then transferred to RH_w using the parameterization of saturation pressures for ice and liquid water given by Murphy and Koop, 2005. As this plot provides a supplementary comparison of our measurements in another parameter space, but is not crucial for the discussion, we decided to put this figure in the appendix and added the following figure description:

Figure C1. Summary of homogeneous freezing measurements of H_2SO_4/H_2O solutions in the a_w-T-space. The homogeneous freezing onsets of sulfuric acid solution samples shown in Fig. 1 are complemented by the AIDA results from this study (red points). The results in the S_{ice}-T-space were converted into the a_w-T-space by assuming equilibrium conditions $a_w=RH_w$ and by using the parameterizations for the water vapor saturation pressures with respect to ice and supercooled liquid water given by Murphy and Koop (2005). The uncertainties of the calculated a_w values vary between ±0.036 and ±0.076.

We referred to this figure in the Section "3. Results and discussion", as follows:

With decreasing temperature, the AIDA measurements show an increasing deviation from Koop2000 towards higher ice saturation ratios.
A comparison of the AIDA results to the homogeneous freezing onsets from previous studies in the a_w-T-space shown in Fig. 1 can be found in Fig. C1.

- There is a lot of uncertainty in the estimation of aw at low T. Slow droplet growth is not a sufficient condition to rule out kinetic limitations since the formation of glasses and hydrates is possible. The E-AIM model does not account for curvature effects which may bias the aw estimate as well.

We added the following sentence to the introduction, where the E-AIM model is mentioned the first time. We also added the Koop, 2004 reference, where this kind of uncertainties are further described:

It needs to be considered that for the low temperature range, the model predictions are based on extrapolations of physiochemical properties towards low temperatures, which remain uncertain (Koop, 2004).

We also added this reference to the Section "3. Results and Discussion":

The descriptions for the liquid water saturation pressures are rather uncertain **(Koop, 2004)**, and existing parameterizations deviate from each other (e.g. Buck, 1981; Sonntag, 1994; Tabazadeh et al., 1997; Murphy and Koop, 2005; Nachbar et al., 2019).

We fully agree that the uncertainty of the determination of the water activity at low temperature is an important issue. Our study shows that the conversion of data from different experimental set-ups like the AIDA chamber to compare with the WAC brings uncertainties into the description of homogeneous freezing. For this conversion, calculations based on parameterizations for e.g. water activities of different solutes and the water vapor saturation pressure with respect to supercooled liquid water are needed, which are uncertain especially at low temperatures. More details on this discussion are given in the responses to the major comments 1 and 3 of referee #1.

- The single experiment shown ruling out kinetic limitations is performed at 197 K hence does not target the conditions where the discrepancy with Koop2000 is the largest. It is my feeling that all experiments should have been conducted allowing for equilibration time in the same way as depicted in Fig. 5.

Please note that the experiment shown in Fig. 5 was started at 197 K, but the actual ice onset temperature was observed at a lower temperature of about 193 K with a corresponding ice saturation ratio of about 1.95. Therefore, this experiment was done in the temperature regime, where the observed deviation in onset supersaturation is already significant and we consider it as representative for the other experiments with significant deviation. We are planning more AIDA homogeneous freezing experiments with other solutes and will take up your suggestion to carry out more experiments with variable pumps speeds or rate of pressure change.

- One assumption of Koop2000 is that aw is independent of temperature. Deviation from this behavior would be enough to explain the discrepancy against the results of this work.

Only for some of the experiments shown in Koop et al. (2000), the water activity of the solution aerosols was determined by assuming that a_w is independent of the temperature. In Fig. 1b, Koop et al. (2000) distinguish between freezing points, for which the water activity was derived directly by an ion interaction model at the actual freezing temperature (filled circles), and for which the water activity was estimated by equalling a_w to that measured at the melting temperature (open circles), thus assuming that a_w is independent of temperature between the melting and freezing temperature. All data points are well represented by the shown fit line, independent of the method by which the water activity was determined. We therefore cannot state that the temperature dependence of a_w is generally not taken into account, but, as outlined above, have pointed to the overall uncertainty of the E-AIM in estimating a_w at low T in the revised manuscript version.

- What would happen with the sulfuric acid upon freezing in highly concentrated droplets? This is significant since a fundamental assumption of the equilibrium approach to ice nucleation is that aw=1 in ice. Does the acid remain at the center of the droplet or does it get pushed to the surface (as another review notes, there is some evidence for the later)? If it is incorporated in the ice lattice, then the equilibrium calculations must be corrected accordingly.

Unfortunately, we cannot derive from our measurements what exactly happens to the acid when the ice forms and how it is distributed in or around the ice lattice. There are observations and theories claiming that the remaining highly concentrated sulfuric acid completely covers the ice crystal during the initial growth of the critical ice nucleus, which may decelerate ice crystal growth and could therefore explain the observed high freezing onset supersaturations (e.g. Bogdan et al., 2010). This way of kinetic limitation is also discussed in the manuscript in Section "3. Results and discussion". This discussion was improved and extended with more details, please see our response to major comment 3 of referee#1 for the changes and additions to the manuscript.

- The authors assert that their new correlation should be used instead of the Koop2000 However homogeneous ice nucleation does not admit a "singular" description, and the definition of a freezing threshold is of limited use for atmospheric modeling. Enough data is available in the experiments to calculate the nucleation rate. This would be more meaningful and useful. It would also refute/corroborate the Koop2000 approach of estimating the nucleation rate of solutions at low T based on that of pure water at much higher T. Does the Koop2000 parameterization for J match the measured nucleation rate? This would be a much better test of the Koop2000 hypothesis than the mere calculation of the freezing threshold.

We understand that the application of the new fit line for the sulfuric acid AIDA data in atmospheric models should not be used suggested. We therefore removed any statement suggesting this and added some notes of caution when applying the fit line to atmospheric conditions. For details on the changes in the manuscript, please see the responses to referees #1 (major comment 4) and #2 (major comment 4).

Our experiments at the AIDA chamber are not designed to explicitly calculate nucleation rates with a high accuracy, which would be needed to describe the dependence of water activity on the nucleation rate coefficient, as it is done in Koop et al. (2000). Möhler et al. (2003) give an estimate of homogeneous freezing nucleation rates to which the determination of the freezing onset in AIDA experiment is sensitive. The article also discusses the uncertainties of this estimation, including the estimation of the freezing probability, which is prone to uncertainties of the ice crystal number determination, the estimation of the volume of particles which freeze, and the uncertainty of the time determined for the occurrence of the freezing onset. Therefore, we can only provide an upper and lower limit of nucleation rates to which the AIDA measurements are sensitive to. Based on this estimation in Möhler et al. (2003), we compared our AIDA results to the WAC-lines for the given range of nucleation rates. Due to the mentioned uncertainties, a more accurate determination of nucleation rates is not possible with our experimental set-up.

Technical comments

Line 13. Please spell out "several thousand"
Corrected.

Line 31. Organic monolayers also promote freezing, not only solid ice-nucleating particles.
We changed the sentence as follows:
In regions with low concentrations of ~~solid~~ ice-nucleating particles, […].

Line 50. This is probably backwards. Higher aw leads to higher J in the Koop2000 model.
Corrected as follows:
Also shown are homogeneous freezing onset lines calculated according to Koop2000 for nucleation rate coefficients of $J_V = 10^{13}$ $cm^{-3}s^{-1}$ ($\Delta a_w = 0.3$**2**, dashed line) and $J_V = 5 \cdot 10^8$ $cm^{-3}s^{-1}$ ($\Delta a_w = 0.3$~~2~~, dotted line) (Möhler et al., 2003).

Line 129. At least for these experiments the FTIR data should give some insight on whether the equilibrium assumption is correct. Does the aw calculated with the E-AIM model using the measured mass concentration match the relative humidity in the cloud chamber?
An accurate analysis of the FTIR data would in principle even be much more insightful, as it could provide the composition of the solution droplets (wt% H_2SO_4) upon freezing, i.e. the same quantity as inferred from the freezing experiments by Koop et al. (1998) with deposited sulfuric acid solution droplets. However, due to the lack of accurate infrared optical constants of dilute sulfuric acid solution droplets at such very low temperatures, this analysis is affected by a large uncertainty. It can be seen in the compilation of Fig. 1 in the manuscript that previous studies that have employed infrared spectroscopy to analyze the freezing of H_2SO_4/H_2O aerosol particles (e.g. Bertram et al., 1996 and Clapp et al., 1997) show large deviations from the WAC line, probably due to uncertainties in the determination of the composition of the solution droplets at the freezing onset (Koop et al., 1998). Since 1997, some new low-temperature refractive index data sets for H_2SO_4/H_2O have been published, and we have used them in Wagner et al. (2008) to develop an approach to quantitatively analyze the dilution of the sulfuric acid solution droplets during expansion cooling in the AIDA chamber and determine their composition prior to freezing. However, these new data sets still do not fully capture the range of temperatures and compositions covered by our expansion cooling experiments, so that the analysis remains highly uncertain. Generally, the a_w calculated with the E-AIM model using the droplet composition estimated from the FTIR measurements is 20-30% smaller than the measured relative humidity. But this might again be due to uncertainties in the E-AIM calculations and the saturation water vapor pressure parameterization and cannot be taken as an argument that the equilibrium condition is incorrect.

Line 137. Typo in “aerosol”.
Corrected.

Line 165. How important is the Kelvin effect overall? The E-AIM model does not account for it.
For our AIDA experiments, we assume that the Kelvin effect is not contributing to the observed freezing behavior, as the majority of the injected aerosol particles generally were larger than 100 nm in diameter. From the mentioned process modelling studies (Haag et al., 2003 and Wagner et al., 2008), we learned that smaller particles, which are affected by the Kelvin effect, do not maintain the same equilibrium compositions as the larger particles in the aerosol population. Consequently, their freezing behavior should be affected if the water activity is crucial for the homogeneous freezing onsets.

Line 176. Is there an induction time between the onset of ice and the observation a rozen droplet? In other words, how long does it take for ice to propagate inside a droplet?
In general, the diffusive growth of an ice particle is very fast. Of course, it is important to show that this is also the case for low temperature experiments. In the response to major comment 3 of referee #1, we calculated the diffusion length for a water molecule on a time scale of 6s. This diffusion length is significantly larger than the mean particle

diameter in all the experiments. This indicates that the diffusion of water in the aerosol and therefore the growth of the initial ice nucleus is fast. An additional indication that the ice growth is very fast also at low temperatures is the experiment we show in Fig. 5 in the manuscript. Here, we can see that in the minutes of constant but high relative humidity, no ice is detected. This would be the case, if the ice onset already happened at or below this relative humidity, but the detection of the formed ice particles would be delayed due to a significant induction time. In addition, the relative increase in the activated fraction and depolarization (third panel in Fig. 5) is strong and comparable to the increase observed in the experiments at higher temperatures. Regarding our OPCs, their detection range starts at about 0.7 µm. As discussed in Järvinen et al. (2014) the OPCs overestimate the size of aspherical ice particles by a factor of about 2.2. This means that an initial ice embryo needs to grow to an ice particle with a diameter of about 0.32 µm. In our uncertainty analysis, we considered the change in relative humidity and temperature in a specific time interval. Based on the diffusion lengths estimated above, this time interval is expected to cover the time the ice crystal needs to grow in the detection range of the OPC. This is also supported by the observation that the ice onsets determined by the OPCs agree well with the onsets determined by the light scattering measurements of the SIMONE instrument (see Fig. A1 in the manuscript). Therefore, a potential induction time is not expected to change the determined ice onsets in the given uncertainty range.

We added a statement on the potential induction time to Section "2.4 Analysis of uncertainties":

We determined an uncertainty of ±3 s for the onset time. **Based on estimates for the diffusion length of water molecules in the H_2SO_4/H_2O aerosol particles at low temperature, which are discussed in greater detail in Sect. 3, we assume that this uncertainty covers the time the initial ice nucleus needs to grow into the detection range of the OPCs.** The variability of the gas temperature T in this 6s time interval is a first factor contributing to the uncertainty of T_{ice}.

Line 203. Please define the freezing probability.
We added the following to the text in the manuscript:
These nucleation rate coefficients were determined for sulfuric acid aerosol particles with diameters between 0.5 and 2 µm with an estimated freezing probability between 0.02 and 0.5. **For the definition of the freezing probability, see Eq. 2 in Möhler et al. (2003).**

Line 204. Given that the whole nucleation "pulse" lasts about 100 s this time delay could be significant.
In the AIDA experiments, we do not have a kind of "nucleation pulse". Temperature is decreasing during the experiment run and the relative humidity is increasing accordingly, until a specific nucleation rate is reached, which causes the observed ice onset in the chamber. This ice onset is characterized by the current temperature and relative humidity inside the chamber. At lower temperatures, the relative humidity changes more slowly over time, so that the uncertainty of ice onset relative humidity is reduced.

Line 252. Please spell out "several thousand" or rephrase it.
Done.

Line 272. This is a key line. Do the authors suggest that such is not the case? If aw-awi is not constant, then the Koop2000 approach is not valid at these conditions. If this is what the authors meant, please spell it out.
No, we do not want to suggest that it is not the case, that the nucleation rate coefficients can be described only in dependence on water activity and temperature. As already stated in our response to referee #1, we do not want to suggest that the WAC and the

underlying assumptions are not correct. Instead, we want to show that the conversion of data from different experimental set-ups like the AIDA chamber to compare with the WAC brings uncertainties into the description of homogeneous freezing. For this conversion, calculations based on parameterizations for e.g. the water vapor saturation pressure with respect to supercooled liquid water are needed, which are uncertain especially at low temperatures.

Line 288. This is a large uncertainty. What is the equivalent in aw space?
The uncertainties of S_{ice} converted into the a_w-space gives uncertainties of a_w between ±0.036 and ±0.076. This is also plotted in Fig. C1, which has been added to the manuscript appendix, and mentioned in the figure description.

Line 316-320. I don't see how these results indicate no internal kinetic limitations or that there is no induction time. In fact, in Line 204 it was indicated that it could be as much as 10 s. All that the experiment does is to show that droplet growth is slow (which could be due to glass formation) before nucleation, not that the equilibration time scale is much smaller than the nucleation time scale. Please explain.

We added a more detailed discussion on the kinetic limitations and phase state of the sulfuric acid aerosol particles to Section "3. Results and discussion". Please see response to major comment 3 of referee#1.
We also added a more detailed description of the mentioned experiment shown in Fig. 5 in the manuscript including a new additional panel showing a direct comparison of the relative humidity and the forward scattering intensity measured by SIMONE. We do not agree that the experiment shows that the droplet growth is slow. Rather, the additional panel emphasizes that the particles react instantaneously to the changes in relative humidity. As soon as the pumping speed is reduced and the relative humidity is controlled for a duration of about 300 s to a constant value clearly above the Koop et al. (2000) line, there is no further increase of the forward scattering intensity, which could be ascribed to a delayed water uptake. Rather, the scattering intensities instantly follow the smooth variations in the relative humidity. This observation (which is now much better described in the revised manuscript version), together with the estimates for the diffusion length of the water molecules in the H2SO4/H2O aerosol particles, indicates that kinetic limitations of the particles growth due to water uptake are not expected during the experiment.

Line 321-323. How does the aw calculated with the measured mass concentration compare against the relative humidity? Does the equilibrium assumption hold?
Please see the response to the comment to line 129 above.

Line 340. Freezing thresholds are not very useful for atmospheric modeling. The authors should report nucleation rates instead.
Please see the response to the last general comment about the difficulty of calculating nucleation rates with high accuracy from the AIDA experiments.

Line 345-355. This is confusing. Please just report the recommended correlation.
We decided to keep the unconstrained version of the fit and removed the constrained one from Fig. 6 and the corresponding text. For details on the changes made in the manuscript, please see the response to the minor comment 8 of referee#1.

Line 385. There is the implicit assumption that the nucleation rate is still a function of aw only, which seems to contradict the premise of this work.
At first, we decided to remove the constrained fit, which is described in this line, and to only keep the unconstrained one, as it was suggested to only keep one of the fit

versions. However, in general, the assumption that the nucleation rate coefficient is still a function of Δa_w as suggested by Koop et al. (2000), does not contradict the conclusion and discussion of this study. Rather, we show that we observe deviation from the WAC-derived homogeneous freezing lines, but relate this deviation to the conversion from different parameter spaces into each other, and not to an invalidity of the ideas behind the WAC. See also our answer to line 272 above.

Line 392. There is not enough data here to assert this. Koop2000 also parameterizes nucleation rates which is much more useful and completely omitted in this work.
We understand that it should not be suggested to replace the well-established Koop2000 freezing lines. We therefore adjusted this section in the manuscript as follows:

Consequently, a precise description of homogeneous freezing processes is crucial to understand cloud radiative effects in the present climate as well as in predictions of climate change. ~~The new parameterization suggested here may be used as a replacement of the Koop2000 homogeneous freezing onset lines.~~ This may in particular be relevant for cirrus clouds in the cold tropical tropopause layer
(TTL). (This section was moved from Section "4. Conclusions" to Section "3. Results and discussion")

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