

Responses to editor and referee comments:

We thank the editor and the referees again for their thoughtful 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.

Editor report:

Dear Authors,

I received the comments of the referees on your revised version of the manuscript. Those are listed below with further comments of mine. Please address my and the referees' minor comments before proceeding with the publication of this work.

With kindest regards,

Daniel Knopf

Dear Daniel Knopf,

Thank you for carefully reading again the revised manuscript and for your comments. Please find our answers below.

Best regards, on behalf of all authors,

Julia Schneider

Editor minor comments:

You added uncertainties to the freezing line in Figs. 4 and 6. I just want to clarify that this is not an uncertainty of $\pm 5\%$ but is ± 0.05 error in water activity. Hence, it will scale slightly with temperature, I believe. Could you please indicate the meaning of the shading in the respective figure captions. Plotting this uncertainty in Fig. 1 as parallel lines to the Koop et al. (2000) freezing curve would be beneficial/fair showing that this includes many of the experimental data points.

We corrected the shown uncertainties in Fig. 4 and 6 in the manuscript so that they now actually represent a relative uncertainty of $\pm 5\%$ in water activity as given in Koop (2004), and added an explanation on the shaded areas to the figure descriptions. Please see revised figures and changes in the figure descriptions below.

We also added the uncertainty range in water activity of $\pm 5\%$ to the Koop lines shown in Fig. 1 and in Fig. C1 according to Fig. 9 in Koop (2004) and adjusted the figure descriptions in the manuscript (see changes below).

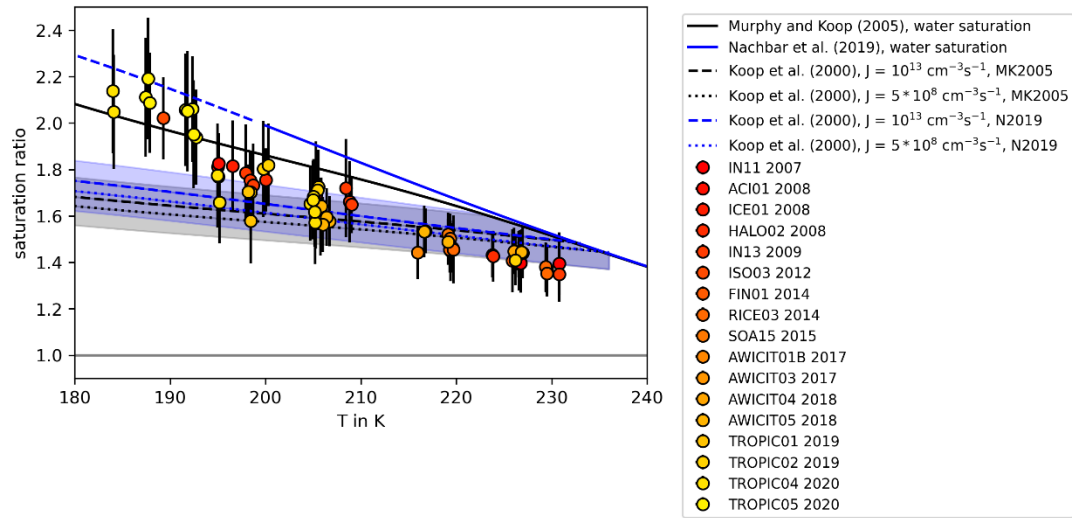


Figure 4. Homogeneous freezing onsets of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ aerosol particles. The freezing onset conditions, T_{ice} and $S_{\text{ice,fr}}$, are displayed in comparison with the homogeneous freezing thresholds suggested by the WAC-based predictions by Koop et al. (2000) (dashed and dotted lines) using two different parameterizations for the water saturation pressure with respect to supercooled liquid water from Murphy and Koop (2005) (MK2005, black) and Nachbar et al. (2019) (N2019, blue). **The blue and grey shaded areas are indicative for the uncertainties of the WAC-based predictions ($\pm 5\%$ in water activity) as given in Koop (2004).** The used water saturation pressures with respect to supercooled liquid water according to MK2005 (solid black line) and N2019 (solid blue line) are also shown. The colors of the measurement data points represent the different AIDA campaigns in the corresponding years. The oldest campaigns are presented in reddish, whereas the more recent campaigns are shown in yellowish colors.

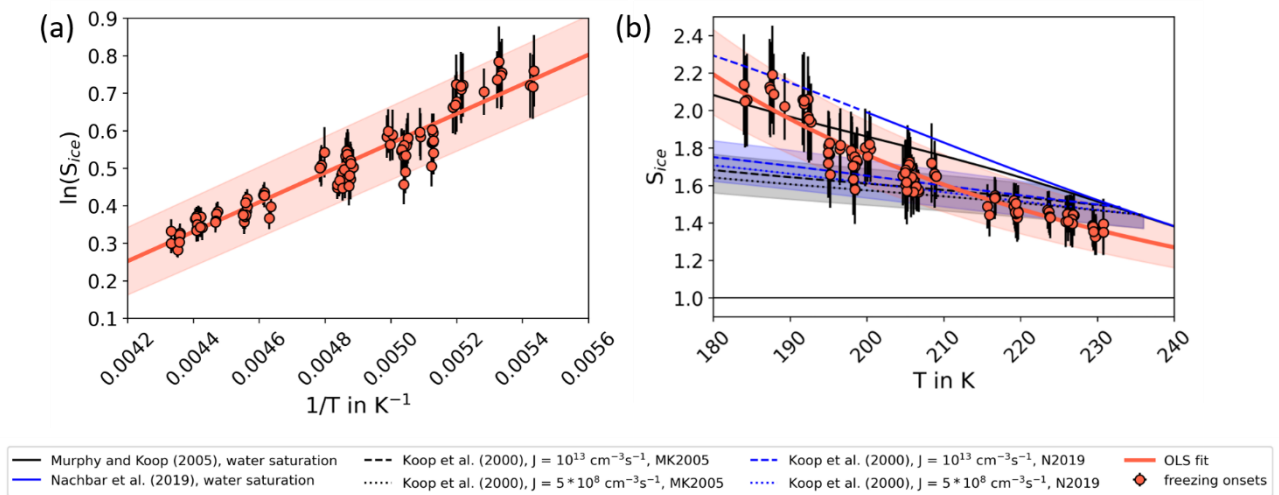


Figure 6. New fit line for homogeneous freezing onsets of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ aerosol particles. Panel (a): The freezing onsets determined by OPC and SIMONE data (red dots) are shown in an Arrhenius plot and fitted by an ordinary least square (OLS) fit with the form $\ln(S_{\text{ice}}) = a + 1/T \cdot b$. The parameters are $a = -1.40 \pm 0.05$ and $b = 390 \pm 10 \text{ K}$ and the goodness of the fit is $R^2 = 0.92$. The shaded area is indicative

for the uncertainty of the fit parameters. **Panel (b):** The OLS fit shown in panel (a) is transferred into the S_{ice} -T-space and compared to Koop2000 and the water saturation lines suggested by Murphy and Koop (2005) and Nachbar et al. (2019). The blue and grey shaded areas are indicative for the uncertainties of Koop2000 ($\pm 5\%$ in water activity) as given in Koop (2004).

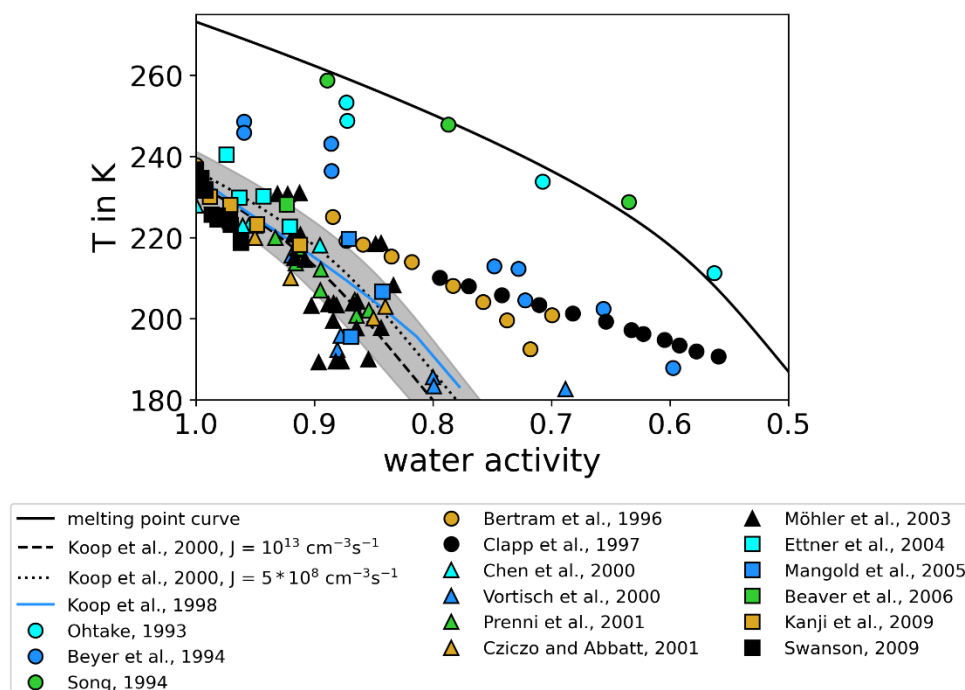


Figure 1. Review of homogeneous freezing measurements of H_2SO_4/H_2O solutions. The homogeneous freezing onsets of sulfuric acid solution samples reported in different studies are shown and compared. Most of the studies report onset temperatures and weight percentage of H_2SO_4 in the solution samples. We used Model I of the E-AIM model (Clegg et al., 1992; Carslaw et al., 1995; Massucci et al., 1999; Wexler and Clegg, 2002; Clegg and Brimblecombe, 2005) to transfer this weight percentage data into water activity, which is assumed to be equal to the relative humidity (assumption of thermodynamic equilibrium). If ice saturation ratios were given, the parameterizations of Murphy and Koop (2005) for the saturation pressures of supercooled liquid water and ice were used to calculate water activities. Additionally, the melting point line according to Murphy and Koop (2005) (solid line) and the homogeneous freezing thresholds for two different nucleation rate coefficients according to Koop et al. (2000) (dashed and dotted lines) are shown. **The grey shaded area is indicative for the uncertainties of these homogeneous freezing thresholds ($\pm 5\%$ in water activity) as given in Koop (2004).**

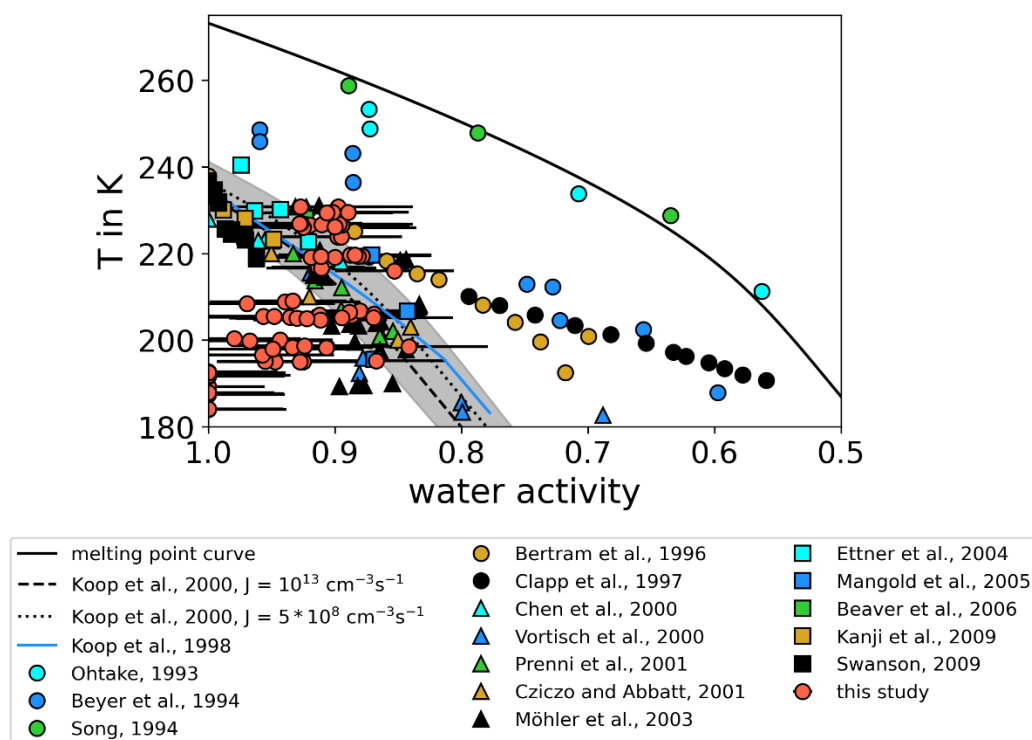


Figure C1. Summary of homogeneous freezing measurements of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solutions in the a_w -T-space. The homogeneous freezing onsets of sulfuric acid solution samples shown in Fig. 1 are complemented by the AIDA results from this study (red points). The results in the 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 .

Something not discussed by the referees: The homogenous ice nucleation rate coefficient is likely overpredicted by Koop et al. (2000)¹. Knopf and Rigg (2011)² suggested that J_{hom} is likely about 2 orders of magnitude lower. This was also observed in a study by the Koop group (Riechers et al. 2013³). This could delay ice nucleation or decrease the number of ice crystals to be observed. There is no need to go into detail with this but it may be worthwhile to briefly mention the role of J_{hom} .

We added a statement on the homogeneous nucleation rate coefficient and its impact on the Koop2000 lines to Section “3. Results and discussion” including the suggested references. Changes in the manuscript as follows:

The Koop2000 lines are based on homogeneous freezing experiments of 18 different aqueous solutions with a known and constant composition. The homogeneous freezing temperature was measured as a function of the concentration of the solute. Converting the solute concentration into water activity resulted in a close match of the freezing temperatures for the different solutes. It was therefore suggested to formulate the freezing nucleation rate coefficients of aqueous solution particles only as function of the water activity and the temperature. **More recent studies suggested that the homogeneous nucleation rate coefficients are about 2 orders of magnitude**

lower than those given by Koop et al. (2000) (Knopf and Rigg, 2011; Riechers et al., 2013). In terms of water activity, the experimentally derived freezing curve by Knopf and Rigg (2011) is about 0.01 lower than that predicted by Koop et al. (2000). This slightly delayed ice nucleation onset, however, does not account for the much larger deviation of the AIDA results to Koop2000.

Reviewer comments (I have an additional comment to reviewer #3):

Reviewer #1:

The authors have responded well to the comments and I applaud them for their efforts. I recommend publication after a few technical comments listed below are addressed.

1) I. 328-329 revised text. Again, this statement is not entirely accurate because hysteresis is not completely considered. Glassy particles will transition over time to a more well-mixed dilute particle. This could last 1600 s starting at 215 K and cooling to 212 K as reported in my previous comment. Their experiments last < 600 s and maybe I missed this, but how long do the particles wait at the "starting" conditions? During the glass-aqueous solution transition, the particle will still not be in equilibrium as the glassy core is not transitioning. Strictly speaking, just because water uptake occurs does not mean particles are not glassy.

The aerosol particles were exposed to the starting conditions for at least 20 min. We agree that the mere water uptake does not rule out the possibility that the particle core could still be glassy. But we have now better described the time series of the SIMONE data during the considered experiment (see new panel 5b), and explicitly pointed out that there was also no delayed water uptake when the RH was temporarily controlled to a constant value, which contradicts the assumption of a gradual glass-aqueous solution transition.

We therefore propose to delete the corresponding sentence and to combine it with the previous one as follows:

This is also supported by the aerosol particle forward scattering intensity measurements with the SIMONE instrument, which **showed no evidence of delayed water uptake that would be expected if initially glassy particles were gradually transformed to aqueous solution droplets.** ~~an increasing signal between pump start and ice onset for all the experiments. This increase shows that the aerosol particles take up water and dilute, which would not be expected for glassy particles.~~

2) References: Many have chemical formulas that require subscripts. Please check.

Corrected.

3) References: Please check Czikzo et al. 2013. "(80-.)".

Corrected.

4) References: Please check the last author in the list for Vortisch et al. 2000.

Corrected.

Reviewer #3:

I thank the authors for addressing my comments and clarify the uncertainties of their approach.

However there is still one thing that is bothering me quite a bit.

I asked the authors to plot their results in the same way as Koop et al. 2000 (that is T_f vs a_w). They did it as Figure 1 in their response (AC3). But something seems quite odd. The other studies tend to underestimate a_w against Koop2000, however this study overestimates it. Moreover, below 200 K all their a_w values are above 1. Honestly I can't think of a scenario where a highly concentrated solution of sulfuric acid would have $a_w > 1$. I would like the authors to please clarify this, just to make sure their analysis is fundamentally consistent.

Editor comment: Reviewer #3 refers to Figs. 1 and C1. To put it in other words and to avoid confusion that persists in the community and literature: Obviously, RH is a parameter that describes the gas phase and a_w the condensed phase. If gas and condensed phase are in equilibrium, $RH = a_w$. Although in experiments one can achieve $RH > 100\%$, a_w can never be larger than 1. $a_w = 1$ indicates the presence of pure water, not bound to other ions etc. Even if the gas phase rises above 100% RH and more water condenses, a_w stays equal to 1.

We agree with referee #3 and the editor that a water activity > 1 cannot occur. We have therefore adjusted Fig. 1 and Fig. C1 by setting those data points, at which the measured S_{ice} onset corresponded to a relative humidity $> 100\%$, to a water activity equal to one. As noted above, we also included the uncertainty range of the Koop et al., 2000 lines. For changes in the manuscript, please see the revised Fig. 1 and C1 and descriptions above. Please note again that the water activities for the new AIDA experiments plotted in Fig. C1 only result from the conversion of our directly measured nucleation onsets, given in terms of $S_{ice}(T)$. We also do not expect that the water activities of the aqueous sulfuric acid solution droplets (which have a concentration of about 25 wt% H_2SO_4 when freezing at 190 K) have values close or equal to one, as suggested by the AIDA data for temperatures below 200 K. Rather, we discuss in our article that the uncertainty with respect to the parameterization for the saturation water vapor pressure over supercooled water at $T \leq 200$ K could be a reason for the apparently “inconsistent” picture when our $S_{ice}(T)$ freezing data are converted to the $a_w(T)$ space in Fig. C1 (see also the point below). For that reason, we provided our parameterization directly in the measured $S_{ice} - T$ space.

The other point the reviewer hints to when asking for “fundamentally consistent” is: If you plot a data point indicating pure water ($a_w = 1$) below ~ 235 K (Fig. C1), you imply the existence of water/ice in the physical not allowed region, also called “no man’s land” (see your Fig. D1). With the experimental conditions applied here, you cannot produce ice under these thermodynamic conditions. This in turn implies that the water saturation parameterizations (both Nachbar et al. and Murphy and Koop) would need to make a huge jump to higher RH_{ice} values below 200 K to make this somehow consistent with known physics.

We agree that it is difficult to show and discuss freezing experiments in the “no man’s land” region. However, we think a discussion of measurements at these conditions is important, as these occur in the upper troposphere/lower stratosphere. We agree that the water saturation parameterizations are a critical aspect in this discussion, as we also state in Section “3. Results and discussion”. Nachbar et al., 2019 do not give a parameterization for water saturation pressure below 200 K and the Murphy and Koop, 2005 parameterization is based on interpolations through the “no man’s land” region. This shows how uncertain the parameterizations at these conditions are. Nachbar et al. (2019) actually suggested that there could be a discontinuity in the water vapor pressure in the “no man’s land” region between 230 and 200 K, because their findings indicate that amorphous solid water (ASW) and supercooled liquid water (SLW) are distinct phases of water, potentially involving a

phase transition somewhere in the “no man’s land”. As shown in their Fig. 2, there is a large gap between the water vapor pressures at 200 K (the warmest known temperature of existence of ASW) and 236 K (the coldest known temperature of existence of SLW). They proposed studies of the condensation of gas phase water on hydrophobic surfaces to detect a potential phase transition from SLW to ASW when lowering the temperature, and as stated in the article we plan to focus on this aspect in future experiments.

Clearly, there are processes in the aqueous sulfuric acid system going on below 200 K that we do not completely understand. The only other point that has not been mentioned is that the aqueous sulfuric acid aerosol may transform into a sulfuric acid monohydrate which happens slightly above 190 K (considering the uncertainty in RH, there might be a range where this could happen). See, e.g., discussion of Fig. 6 in Koop et al. (2011)⁴. Then some water would be bound in the crystal with a remaining aqueous solution outside the crystal yielding a much decreased aw value. This could potentially reduce the disagreements observed below 200 K.

The potential crystallization of sulfuric acid hydrates (e.g. the monohydrate, SAM, or the tetrahydrate SAT) and their impact on the ice nucleation experiments at temperatures below 200 K is indeed an interesting question. Our measurement data do not indicate that such crystallization has occurred in a significant (> 5-10%) number fraction of the injected aerosol particles. Firstly, sulfuric acid hydrate infrared spectra have features distinctly different from aqueous H₂SO₄/H₂O solution droplets (Nash et al., 2001), but such signatures were not detected in our FTIR measurements. Secondly, the presence of crystalline or partly crystalline particles would have resulted in an increase of the backscattering linear depolarization ratio compared to the background value measured for purely aqueous solution droplets, which was also not detected in the SIMONE records. Thirdly, as shown specifically for SAT (Fortin et al., 2003), sulfuric acid hydrates could act as ice nucleating particles and induce heterogeneous ice formation at lower S_{ice} values compared to homogeneous freezing conditions, which was also not detected in the experiments presented in this article. We therefore strongly suppose that our experiments were unaffected by the formation of hydrates, and we will add a short statement on this issue in Section “3. Results and discussion” of the article:

[...] In addition, the depolarization measurements with the SIMONE instrument and the signatures of the recorded FTIR spectra show no indication for the formation of sulfuric acid hydrates (Nash et al., 2001), which could occur under the experimental conditions in the AIDA chamber (Koop et al., 1997). An impact of hydrate formation on the observed ice onsets, as shown e.g. in the case of sulfuric acid tetrahydrate (Fortin et al., 2003), is therefore not expected.

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