Review for “High Homogeneous Freezing Onsets of Sulfuric Acid Aerosol at Cirrus Temperatures" by Schneider et al.

We thank referee #1 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.

The manuscript submitted to Atmospheric Chemistry and Physics titled “High Homogeneous Freezing Onsets of Sulfuric Acid Aerosol at Cirrus Temperatures" by Schneider et al. presents new and reanalyzed data on homogeneous freezing of aqueous sulfuric acid aerosol in the AIDA chamber. Homogeneous ice nucleation studies at such large supercoolings is certainly relevant topic and important for atmospheric science. The authors report the onset of ice nucleation to be below water saturation and follow the water activity criterion (WAC) from Koop et al.[1]. However, their results deviate from Koop et al.[1] at 185-205 K. After a thorough uncertainty analysis and clearly stating their assumptions, they conclude that this deviation is significant. They claim that the deviation may be because water saturation curves with respect to ice and water are uncertain and suggest that the estimate by Nachbar et al.[2] instead of Murphy and Koop[3] would cause deviations to decrease. Finally, the authors make a claim about the consequence of their results to ambient cirrus clouds. Overall, the intro, methods and results of this manuscript are well written. The methods are described well and the error analysis is sound. However the discussion needs great improvement. There are major comments that cast the authors conclusions in serious doubt. These have to do with the lack of discussion of the physical evidence for the WAC, the uncertainty for the WAC, the mixing time of the particles, and finally, their suggestion of treating homogeneous freezing for cirrus clouds as only from sulfuric acid. A few minor comments exist. Overall, I cannot recommend publication at this time without significant revision.

Major comments

1. There is a lack of any physical reasoning. The WAC is not an empirical parametrization of aqueous sulfuric acid onset freezing temperatures. It is a physical description of freezing of a variety of solutes at ambient pressure, and of pure water at high pressure[1,4]. In Koop[4], physical evidence is presented that freezing and melting temperatures of pure water at high pressure and highly concentrated aqueous solution at ambient pressure are similar and are the result of similar affects on the water hydrogen bonding structure. To be fair and balanced, if the authors claim their data deviates from the WAC, then they must claim a physical reason for this and independent evidence to support their reasoning. For example, if WAC is solute independent (l. 38-39), why do they suspect sulfuric acid is such a special case? Does the hydrogen-hydrogen radial distribution function[4] of sulfuric acid aqueous solutions deviate from high-pressure water at the same water activity? Does it deviate from other solutes below 205 K at the same water activity, but not deviate at warmer temperatures? If they cannot explain their results physically or come up with a realistic quantitative measure, it is acceptable that the authors include a statement that they do not know a physical reason why such a deviation would occur.

First of all, we would like to state that we present here experimental results after careful discussion and uncertainty analysis, with direct measurements of the temperature and ice saturation ratio at the point of homogeneous freezing onset for aqueous sulfuric acid aerosol particles. That our data deviates from those derived from the WAC-based parameterization by Koop et al. (2000) is an experimental result, and does not require any physical reasoning. Physical reasoning is important and may be helpful when discussing possible reasons for this disagreement, and some are included in the discussion in section "3. Results and discussion", but unfortunately we do not yet have a definite explanation for the observed deviation.
Please note that it is not the aim of this paper to question the WAC itself and its physical explanation, but our data provide strong evidence that there is an increasing high bias of the homogeneous freezing onset to lower temperatures, at least for aqueous sulfuric acid aerosol we used in our experiments.
Indeed, we compare the freezing experiments of a single solute, H_2SO_4, with a freezing line established for a variety of different solutes. However, the results of a previous study by Koop et al., 1998 also focusing on the homogeneous freezing of sulfuric acid aerosol particles shows a good agreement with the WAC-based lines with an universal validity independent on the nature of the solute published later in Koop et al., 2000. We therefore also compare the AIDA sulfuric acid measurements to the WAC-based lines. In summary, with our measurements, we cannot and do not want to show that the WAC and the underlying assumptions are not correct. Instead, we want to show that the conversion of data from different experimental setups 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.

In order to focus the discussion more on the observed disagreement with the WAC-based homogeneous freezing line, and to make it more clear that we do not doubt the WAC for homogeneous freezing in general, we add the following statement to "3. Results and Discussion":

Finally, we do not have a solid explanation for the deviation of the H_2SO_4/H_2O homogeneous freezing thresholds observed in AIDA experiments from the WAC-based homogeneous freezing lines. This deviation may be related to uncertainties in the formulation of physicochemical properties at low temperatures, which are required for the conversion between the Koop2000 parameter space (a_w-T-space) and the AIDA parameter space (S_{ice}-T-space), as described above.

2. There is uncertainty of the WAC that should be included. I appreciate the authors experimental uncertainty analysis, however, they lack the uncertainty analysis for the WAC. They must include the uncertainty in the WAC lines for a fair comparison. Koop[4] claims a uncertainty up to 5% in temperature from the freezing line, which translates to an error close to ±15 K in temperature and ±0.08 in water activity, a_w, at homogeneous freezing temperatures of 185 K. Please check this. In order for a fair comparison with WAC, the

authors must calculate errors on the WAC lines at all temperatures and show them in their figures.

Koop (2004) gives an uncertainty range of +/- 5 % for the water activity in the freezing line in the a_w-T-space. We included this range of uncertainty in Fig. 4 and 6, as a shaded area around the WAC freezing curves.

3. Mixing time of high concentrated aqueous solutions at low temperature. On l. 294, the authors claim their assumption that particles are well-mixed and in equilibrium with their humidified environment. Support for this assumption is given[5] for temperatures > 205 K and for the experiment performed by the authors at 194 K in Fig. 6. However, there remains some doubt about this assumption, and the particles may be highly viscous to the point of limiting mixing within them due to slow molecular transport. Whether a particle is or is not well-mixed can depend on the entire relative humidity history, even before the start of experiments. If experiments began at a relative humidity with respect to ice, RH_i, and temperature in which aqueous aerosol particles were initially in a glassy state, it would take time for a glassy and inhomogeneously mixed particle to transition to mixed and satisfy the authors assumption. For example, Berkemeier et al.[6] has shown that for glassy organic aerosol, a humidity induced transition to well-mixed particles can take 1600 s starting at 215K and cooling to 212 K and consequently humidity increasing from 60% to 87%. Although glassy inorganic solutions may behave differently than glassy organics, experiments by the authors here were 3 to 4 times faster and therefore, a kinetic limitation cannot be ruled out. If the authors began their experiment in Fig. 6 at a lower RH_i as they did for their experiments in Fig. 3, would kinetic limitations be observed? Evidence for a kinetic limitation comes from the sulfuric acid phase diagram[4]. When RH_i = 95% and T = 185 K, the weight percent of sulfuric acid solution in equilibrium is roughly 50%[7{9] and this is exactly at the boundary of ultra-viscous solutions. The authors should include the starting RH_i in the appendix tables.
The uncertainty here is large, of course, due to extrapolation and seen by the scatter in crystallization temperatures of glassy particles upon warming in Fig. 4 of Koop[4]. What I expect is that the authors include a value of viscosity, molecular diffusion coefficients, or mixing time scales at their exact experimental conditions measure in literature. The authors have not shown evidence for this assumption for temperatures down to 185 K. I do not know of existing viscosity or diffusion coefficient measurements in this temperature and humidity range. If they exist, what is the variability. I do not recommend extrapolating from common measurements. A lack of measurements would cast doubt on this assumption, and thus their conclusions.

We agree that the particle phase and the related mixing time at low temperatures are an important aspect to consider in the measurements of this study and that further and more detailed discussion on that is needed.
As a first step, we included the start relative humidity with respect to ice $RH_{i,0}$ and liquid water $RH_{w,0}$ to the tables in the appendix, as suggested.
To illustrate the start conditions and the sulfuric acid phase at the ice onset, we adapted Fig. 4 in Koop, 2004 and added the data points for the start composition of the sulfuric acid aerosol particles in wt% H_2SO_4 for our experiments and the data points for the composition

at ice onset (see Fig. 1 in this response, red and blue dots). The weight percentage composition was determined by using Model I of the E-AIM model with the measured temperature and relative humidity inside the chamber. As described in the referee's comment above, a glassy state of the sulfuric acid aerosol particles in our experiments would strongly influence the observed freezing process due to slow mixing processes. In Fig. 1, we can see that all experiments are above the conditions of ultra-viscous and glassy particles, according to the phase diagram in Fig. 4 in Koop, 2004 and the references therein. Especially the glass transition conditions given in this figure are at significantly lower temperatures compared to our starting and ice onset conditions. This is supported by our SIMONE measurements, which show an increasing signal in the forward scattering intensity between pump start and ice onset, for all the experiments. This increase shows that the aerosol particles are able to take up water and dilute. Only from this observation, it cannot be completely ruled out that an enhanced viscosity at low temperatures decelerates the water uptake, so that it might be not sufficient to maintain particles in thermodynamic equilibrium with the environment. For the investigation of a potential decelerated water uptake, we refer again to the experiment shown in Fig. 5 in the manuscript. In this experiment, the relative humidity was kept nearly constant above Koop2000 for about five minutes. Firstly, we observe no ice formation in this time period, which indicates that the AIDA ice onset is not higher than the Koop2000 line due to a delayed ice detection. Secondly, the forward scattering intensity of the SIMONE instrument (dark red line, third panel) shows a significant increase in the first two minutes of constant pumping, which is related to the water uptake of the particles. In the following five minutes of constant relative humidity (slower pumping), no further uptake of the particles is observed. To illustrate this more precisely, we added a second panel to Fig. 5 in the manuscript (see Fig. 2 in this response), which shows a direct comparison of the relative humidity and the forward scattering intensity on a smaller scale. In this panel, we clearly observe the particle diluting in the first two minutes of the experiment, which generally decreases the particles' viscosity. After that period, the particles could have continued taking up water, but no further increase in the forward scattering is observed, as soon as the pump speed is lowered. Rather, the forward scattering intensity follows nicely the slight variations in the relative humidity, but a decelerated or delayed water uptake is not indicated.

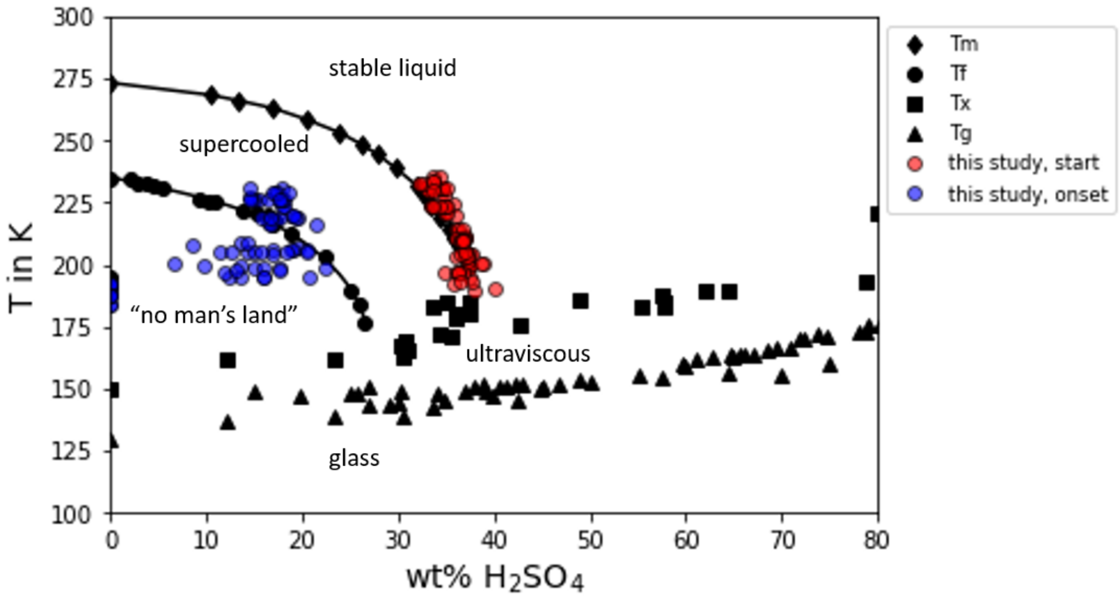

Fig 1: Phase diagram of sulfuric acid adapted from Koop (2004). The phase diagram of sulfuric acid as given by Koop (2004) and references therein is shown and complemented by the calculated weight percentage concentrations of the sulfuric acid aerosol particles before the start of the AIDA experiments of this study (red dots) and at the observed ice onset during the experiments (blue dots).

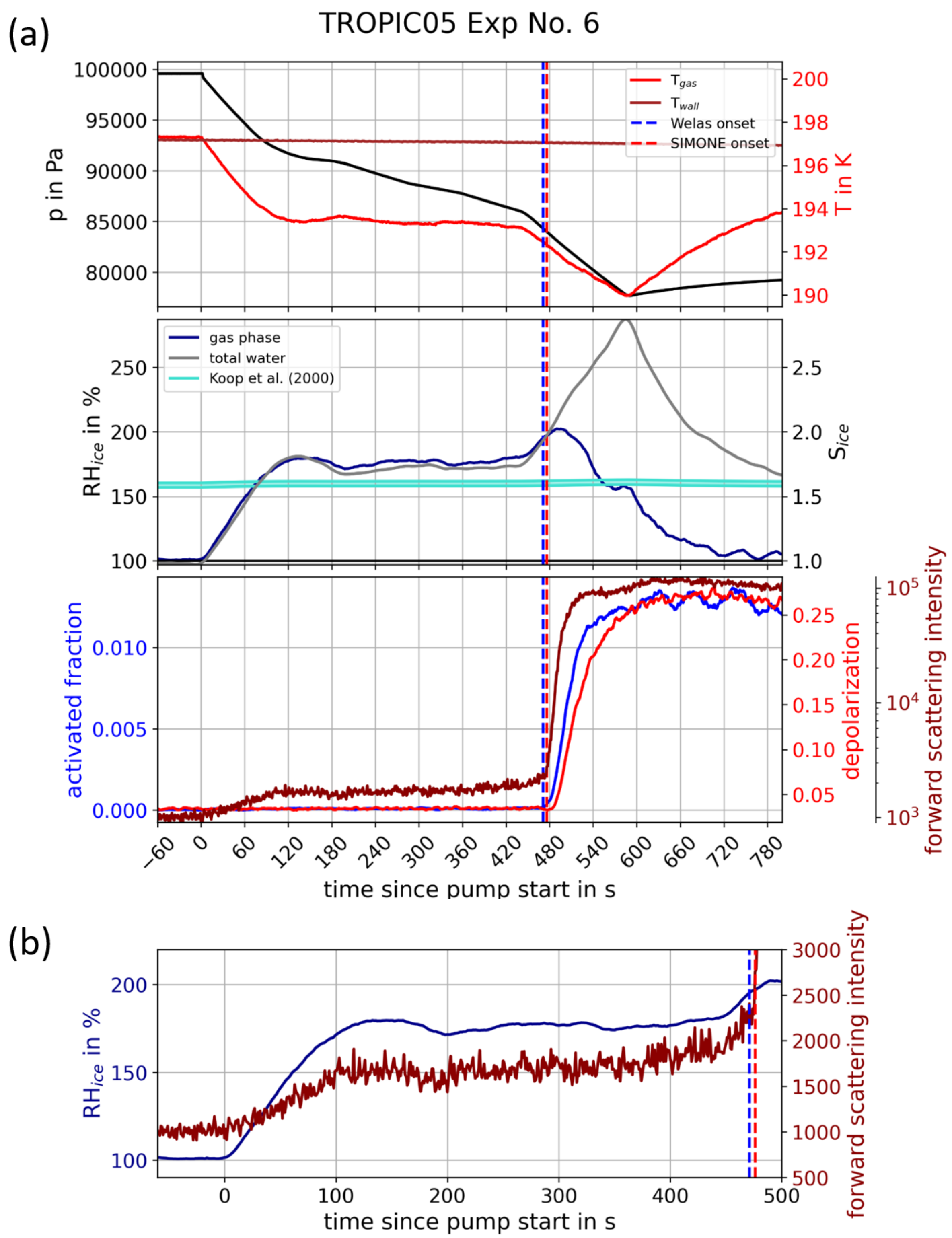

Fig. 2: Investigation of kinetic limitations with respect to water uptake in the AIDA chamber. Panel (a): The figure is composed in the same way as Fig. 3. For the experiment shown, started at about 197K, the pump rate was controlled in such a way that the relative humidity

with respect to ice stayed relatively constant for about 5 minutes at about 170%, hence above the homogeneous freezing threshold suggested by Koop et al. (2000). For details on this experiment, see Sect. 3. Panel (b): Enlarged view of the relative humidity and the forward scattering intensity at the beginning of the experiment.

To our knowledge, studies or measurements of the viscosity of sulfuric acid aerosol particles at very low temperatures are not available in the literature. Measurements and suggested fits for viscosity in dependence on temperature and H_2SO_4 weight percentage concentration by Williams and Long (1995) extend to 200 K and are given for any concentration between 30 and 80 wt%. Fig. 1 in Williams and Long (1995) shows that the viscosity is strongly increasing with decreasing temperature. As the AIDA experiments have weight percentage concentrations < 30% at the ice onset, we can only use the Williams and Long parameterization to determine the viscosity before experiment start when wt% > 30% and for experiments starting at temperatures > 200 K. In Fig. 3a in this response, we show the calculated viscosities η using the Williams and Long parameterization for the AIDA experiments at experiment start (black dots) with start temperatures > 200 K. The viscosities for experiments starting at temperature < 200 K are shown in the grey shaded box, as they need to be treated with caution. In addition, we used these viscosities to determine the diffusion coefficient D of water molecules in the sulfuric acid solution aerosol particles using the Stokes-Einstein-equation (red triangles). With the diffusion coefficients, the diffusion length D_L for a water molecule on a time scale of 6s is calculated and shown in Fig. 3b in comparison to the measured mean diameter of the H_2SO_4/H_2O aerosol particle populations. The diffusion length is significantly larger than the mean particle diameter in all experiments, which indicates that the diffusion of water in the aerosol particles is fast enough to keep them in thermodynamic equilibrium with the environment. Note again that these calculations are only strictly valid for experiments starting at temperatures > 200 K and only for the experiment start conditions.

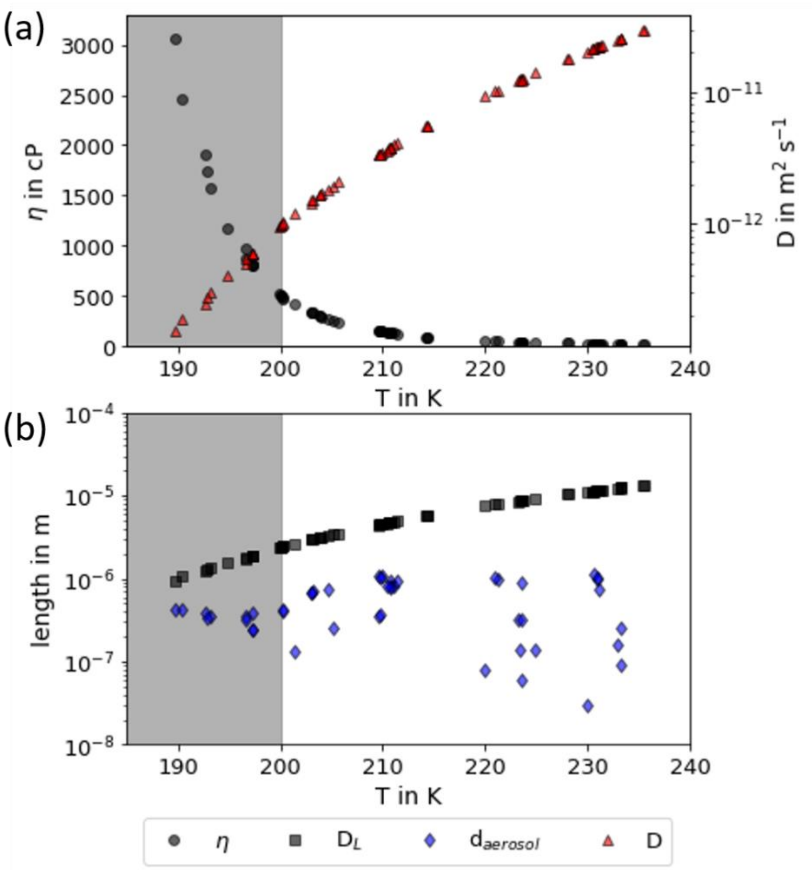

Fig 3: Viscosity and diffusion coefficients for the start conditions of the AIDA experiments. Panel (a): Viscosity (black dots) and diffusion coefficients (red triangles) calculated using the parameterization of Williams and Long (1995) and the Stokes-Einstein-equation. Panel (b): Comparison of the mean particle diameter of the sulfuric acid particle population (blue diamonds) to the diffusion length of water molecules (black squares) on a time scale of 6s. Note that the shown data points represent the starting conditions of the AIDA experiments. As the parameterization of Williams and Long (1995) is only valid for T > 200 K, the data points of experiments at lower temperatures are displayed in a grey shaded box.

We added a similar discussion to Section “3. Results and discussions” and added the Figs. 1 and 3 to the appendix, as additional information, and changed Fig. 5 in the manuscript by adding panel b (see Fig. 2 in this response). Changes in the manuscript are as follows:

For lower temperatures, the viscosity of sulfuric acid increases with decreasing temperature (Williams and Long, 1995) and it can even undergo a transition to a glassy state (Koop, 2004). An enhanced viscosity or a glassy state may reduce the water uptake of the aerosol particles and therefore may delay or inhibit particle growth and dilution. Such effects were discussed to e.g. inhibit homogeneous freezing of secondary organic aerosol particles at T < 200 K (Fowler et al., 2020). For aqueous sulfuric acid solutions, Koop (2004) summarized the conditions for transitions to ultra-viscous and glassy states in dependence on temperature and aerosol composition. To get information about the phase state of the H_2SO_4/H_2O aerosol particles in the AIDA experiments, 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 calculate the sulfuric acid weight percentage for the temperature and humidity conditions before experiment start and at the observed ice

onsets (see Tables B1, B2 and B3). For all experiments, the calculated weight percentages are above the values for a transition to ultra-viscous or glassy particles according to Koop (2004) and references therein (see Fig. D1). In particular, the glass transition occurs at significantly lower temperatures compared to the AIDA starting and ice onset conditions. This is also supported by the aerosol particle forward scattering intensity measurements with the SIMONE instrument, which show 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. To calculate the viscosity of the H_2SO_4/H_2O aerosol particles in the AIDA chamber, we applied the parameterization by Williams and Long (1995). This parameterization is only valid for temperatures > 200 K and for a H_2SO_4 weight percentage between 30 and 80 wt% and can therefore only be applied to the starting conditions of AIDA experiments with T_0 > 200K (see Fig. D2, data points for experiments with T_0 > 200K are displayed in a grey shaded box). The Stokes-Einstein-equation was then used to calculate the diffusion coefficient of water molecules in the aqueous sulfuric acid aerosol particles. From this, we then calculated the diffusion length of water molecules in the aerosol particles on a time scale of 6 seconds, which is much larger than the mean aerosol diameter. This indicates that the water diffusion is still fast enough to keep the aerosol particles in thermodynamic equilibrium.

[…] As soon as the relative humidity is kept at a constant value, no further increase in the forward scattering intensity was observed. **Fig. 5b shows the relative humidity and the forward scattering intensity at the beginning of the experiment. The forward scattering intensity clearly increases during the first two minutes of the experiment, which is caused by water uptake as a result of increasing relative humidity, and results in a decreasing viscosity of the particles. As soon as the relative humidity is controlled to an almost constant value by the reduction of the pump speed, no further increase in the forward scattering intensity is observed. The signal even follows the slight variations in the relative humidity, and a delayed water uptake is not indicated.** This supports our assumption that the aerosol particles can well follow thermodynamic equilibrium conditions during an AIDA experiment at typical pump rates and related rates of cooling and relative humidity increase.

Figure descriptions in the appendix:

Figure D1. Phase diagram of sulfuric acid adapted from Koop (2004). The phase diagram of sulfuric acid as given by Koop (2004) and references therein is shown and complemented by the calculated weight percentage concentrations of the sulfuric acid aerosol particles before the start of the AIDA experiments of this study (red dots) and at the observed ice onset during the experiments (blue dots).

Figure D2. Viscosity and diffusion coefficients for the start conditions of the AIDA experiments. Panel (a): Viscosity (black dots) and diffusion coefficients (red triangles) calculated using the parameterization of Williams and Long (1995) and the Stokes-Einstein-equation. Panel (b): Comparison of the mean particle diameter of the sulfuric acid particle population (blue diamonds) to the diffusion length of water molecules (black squares) on a time scale of 6s. Note that the shown data points represent the starting conditions of the AIDA experiments. As the parameterization of Williams and Long (1995) is only valid for T > 200 K, the data points of experiments at lower temperatures are displayed in a grey shaded box.

Figure description of Fig. 5:

Figure 5. Investigation of kinetic limitations with respect to water uptake in the AIDA chamber. **Panel (a):** The figure is composed in the same way as Fig. 3. For the experiment shown, started at about 197 K, the pump rate was controlled in such a way that the relative humidity with respect to ice stayed relatively constant for about 5 minutes at about 170%, hence above the homogeneous freezing threshold suggested by Koop et al. (2000). For details on this experiment, see Sect. 3. **Panel (b): Enlarged view of the relative humidity and the forward scattering intensity at the beginning of the experiment.**

4. The authors want their fitted line in atmospheric models and replace the WAC (l. 391-392). Inherent in this is that only sulfuric acid aerosol particles nucleate homogeneously to form cirrus clouds in models, is to discard the presence of other solutes such as secondary organic aerosol; nitrates or sea salts, is to treat homogeneous freezing only at the authors' measured onset, and is to not account for homogeneous ice nucleation rate coefficients (as function of water activity and temperature). As there is no given physical explanation for their data, this suggestion is a large leap backward for understanding atmospheric physics and chemistry. The authors certainly make a line go through data points, however it is not appropriate to use this line to predict the formation for cirrus clouds. Up scaling a purely empirical parametrization from the AIDA chamber to real atmospheric conditions is an extrapolation outside of their experimental conditions. If the authors want to replace Koop et al.[1], then more work needs to be done to quantify and understand the physics of homogeneous ice nucleation and apply that understanding to the range of temperature, water activity and nucleation rate coefficients valid for their measurements and consistent with the over 20 years of observation supporting the WAC. Please remove any mention of suggesting to use this parametrization in atmospheric models on l. 344, l. 351-352, l. 384-385 and l. 391-392 and in the last 2 sentences of the **abstract**. These are the instances I have found.

We understand that a replacement of the WAC and the application in atmospheric models should not be suggested. We changed the related sections in the manuscript, as follows:

Abstract:

Based on **the**~~our~~ experimental results **of our direct measurements**, we suggest a new fit line **to formulate** ~~as a parameterization for~~ the onset conditions of homogeneous freezing of sulfuric acid aerosol particles **as an isoline for nucleation rate coefficients between $5 \cdot 10^{8}$ $cm^{-3}s^{-1}$ and 10^{13} $cm^{-3}s^{-1}$**. ~~As a next step, we propose the new parameterization to be implemented in atmospheric models as an improved version of the WAC-based parameterization from Koop et al. (2000). The new~~ **The potential significant impacts of the higher** homogeneous freezing thresholds, **as directly observed in the AIDA experiments under simulated cirrus formation conditions,** ~~may have significant impacts~~ on the **model** prediction of cirrus cloud occurrence and related cloud radiative effects **are discussed**.

Results and Discussion:

Based on the AIDA results and the discussion above, we ~~suggest a new parameterization~~ **provide a new fit line** for homogeneous freezing **of H_2SO_4/H_2O aerosol particles directly measured as function of** S_{ice} and T.

~~In a next step, this fit is constrained to the well-known homogeneous freezing temperature of pure water droplets, so that when applied to atmospheric models it matches the freezing point of pure water droplets (see Fig. 6c and d, red line).~~ (The section about the constrained fit was completely removed.)

~~We suggest to use the constraint fit with the coefficients a = −0.75±0.04 and b = 263±8 K(see Eq. 1 and 6c and d, red line) for use in atmospheric models.~~ **Applying** ~~T~~**t**his **new freezing threshold for cloud formation processes in the atmosphere,** ~~would then result in a shift of~~ the homogeneous freezing onset in cirrus formation **would be shifted** to ice saturation ratios of about 2.0 at temperatures around 185 K. A higher homogeneous freezing onset may explain the high ice saturation ratios **occasionally** reported for low temperatures in the upper troposphere in some field studies (Jensen et al., 2005; Lawson et al., 2008; Krämer et al., 2009; Krämer et al., 2020). **However, it needs to be considered that the fit line only describes homogeneous freezing of H_2SO_4/H_2O aerosol particles under laboratory conditions. Other aerosol species, which could be relevant for homogeneous freezing processes in the atmosphere, are not taken into account. Application to atmospheric conditions therefore needs to be done with caution.**

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")

Conclusions:

A higher homogeneous freezing onset as derived from our experiments may also explain field observations of high clear-sky supersaturation, which should not occur according to the freezing thresholds predicted by Koop2000 (Jensen et al.,2005; Lawson et al., 2008; Krämer et al., 2009; Krämer et al., 2020). **However, the discussed high freezing onsets only consider homogeneous freezing of H_2SO_4/H_2O aerosol particles under laboratory conditions, without involving other atmospherically relevant aerosol species.** ~~We suggest a new parameterization for the homogeneous freezing onset of H2SO4/H2O aerosol particles, which is based on~~ **A**~~a~~n empirical fit to the AIDA results with the form $\ln(S_{ice}) = a + 1/T \cdot b$ with fit parameters a = ~~−0.75±0.04~~ **−1.40±0.05** and b = ~~263±8~~ **390±10** K **describes the observed homogeneous freezing onsets of H_2SO_4/H_2O aerosol particles in the chamber**. **This fit line is based on direct measurements of the freezing onset conditions at simulated cirrus formation conditions and provides an isoline for homogeneous freezing of sulfuric acid aerosol particles for nucleation rate coefficients between $5 \cdot 10^{8}$ $cm^{-3}s^{-1}$ and 10^{13} $cm^{-3}s^{-1}$.** ~~This fit is constrained to the homogeneous freezing temperature of pure water at 235K and water saturated conditions at this temperature.~~ **The application of this fit line to atmospheric conditions requires further work on the physical behavior of H_2SO_4/H_2O**

aerosol particles at low temperatures and on the involvement of other atmospheric aerosol particle types. Ongoing experiments in the AIDA cloud simulation chamber aim at investigating homogeneous freezing onsets of different solutes and at constraining the descriptions for liquid water saturation pressures to experimental results.

Minor comments

1. l. 6. The WAC is not a function of aerosol particle size. Likewise, it is not a function of time either.

We changed the sentence in l. 6 to:
The WAC describes the homogeneous nucleation rate coefficients only as a function of the water activity, ~~temperature and size of the aqueous aerosol particles,~~ which makes this approach well applicable in numerical models.

2. l. 23-24 and 386-407. The authors certainly review and discuss cirrus cloud formation and radiative effects, however, these are not conclusions. No cloud model or any calculations of radiative forcing were made here to support these statements. In the abstract I suggest the following rewrite or something similar, "Our results are discussed in the context of predicting the formation of cirrus clouds and related cloud radiative effects." In addition, these conclusions need to be moved to the results and discussion section.

We changed the last sentence of the abstract to:
~~The new~~ **The potential significant impacts of the higher** homogeneous freezing thresholds, **as directly observed in the AIDA experiments under simulated cirrus formation conditions,** ~~may have significant impacts~~ on the **model** prediction of cirrus cloud occurrence and related cloud radiative effects **are discussed**.

We further moved the section in l. 186-407 from "3. Conclusions" to "4. Results and Discussions".

3. l. 44-47. and 327-329. It was already stated by Koop[4] that thermodynamic models (to calculate water activity of solutions or saturation vapor pressures) extrapolated to these low temperatures can be large sources of errors. I suggest to add this reference here.

Thanks for bringing this reference to our attention. We added the following sentence after lines 44-47:
It needs to be considered that for the low temperature range, the model predictions are based on extrapolations, which remain uncertain (Koop, 2004).

We also added this reference to the other text passages, as suggested:
The descriptions for the liquid water saturation pressures are rather uncertain **(Koop, 2004)**, and ~~various~~ **existing** parameterizations deviate from each other (e.g. Buck, 1981; Sonntag, 1994; Tabazadeh et al., 1997; Murphy and Koop, 2005; Nachbar et al., 2019).

4. l. 46. What E-AIM model did the authors use? I suppose Model I[7{9]. Please check the correct references on the E-AIM website.

Indeed, we used the Model I. We added the correct references, as suggested on the E-AIM website:
In cases where water activities or relative humidities were not given by the authors, we used the Extended AIM Aerosol Thermodynamics Model (E-AIM)**, Inorganic Model I** on http://www.aim.env.uea.ac.uk/aim/aim.php **(Clegg et al., 1992; Carslaw et al., 1995; Massucci et al., 1999; Wexler and Clegg, 2002; Clegg and Brimblecombe, 2005)** to transfer given H_2SO_4 concentrations into water activities, which we assume to be equal to relative humidity.

5. l. 50-51. I think there is a mistake here. Higher values of Δa_w should yield higher values of J_V .

That is right. We corrected this sentence accordingly:
Also shown are homogeneous freezing onset lines calculated according to Koop2000 for nucleation rate coefficients of $J_V = 10^{13}$ cm^{-3}s^{-1} (Δa_w = 0.3**2**, dashed line) and $J_V = 5 \cdot 10^8$ cm^{-3}s^{-1} (Δa_w = 0.3~~2~~, dotted line) (Möhler et al., 2003).

6. l. 61-63. Would the authors take care to please check the ambient ice saturation ratios for these studies? The authors language gives the impression that high RH_i at or above 200% happens all the time at temperatures colder than 200 K. This is misleading. It is directly stated in the abstract Krämer et al.[10] that the highest RH_i for clear sky is about 150%. Krämer et al.[10] shows a distribution of RH_i and there are very rarely any measurements at or above 200%. I count about 7 yellow squares in Fig. 7(e) of Krämer et al.[10] at or above 200%, but practically all data is bounded by or scattered around homogeneous freezing. This statement misrepresents the findings
of Krämer et al.[10], and I would encourage them to be more specific and representative of the previous research they are citing. Please check all citation here. Ambient in-cloud and clear-sky RH_i > 150% occurs mostly < 2% of the time.

We checked the references for the atmospheric observations again and adjusted the text as follows to be more precise:

For T < 200 K, Koop2000 predicts homogeneous freezing thresholds ranging between ice saturation ratios of 1.6 and 1.7. However, **in an aircraft campaign in 2004,** ~~atmospheric observations revealed~~ enhanced ice saturation ratios up to 2.~~0~~**3 at about 187 K were observed in the upper troposphere (Jensen et al., 2005), clearly exceeding the Koop2000 freezing thresholds. Also in a later aircraft campaign in 2006, more than half of the relative humidity measurements showed values exceeding Koop2000 at upper tropospheric temperatures (Lawson et al., 2008). Other atmospheric observations at T < 200 K reported atmospheric relative humidities predominantly below Koop2000, but in a few cases the threshold was also exceeded (Krämer et al., 2009, Krämer et al., 2020). These atmospheric observations** ~~and higher in this temperature range (Jensen et al., 2005; Lawson et al., 2008;~~

~~Krämer et al., 2009; Krämer et al., 2020)~~ seemingly contradict~~ing~~ Koop2000 if the assumption holds that ice saturation ratios are unlikely to exceed the homogeneous freezing thresholds in the atmosphere.

7. l. 334-335. If the Δa_w values would be used together with Nachbar et al.[2] to plot a new onset curve, would everything be within error bars? They claim that difference would be reduced, but why not show these differences and if they can completely explain the deviations they observe.

We added the homogeneous freezing thresholds according to Koop et al., 2000, but with using the parameterization of Nachbar et al., 2019 for the liquid water saturation pressure to the Figs. 4 and 6. We also included the related description and discussion in the text:

This is shown in Fig. 4, where Koop2000 is shown in combination with the liquid water saturation pressure parameterization of Murphy and Koop (2005) (black dashed and dotted lines, MK2005) and additional in combination with the more recent line by Nachbar et al. (2019) (blue dashed and dotted lines, N2019). To fully explain the differences between the AIDA and the Koop2000 onsets, the liquid water saturation pressure would need to be even higher at low temperatures than suggested by Nachbar et al. (2019).

Description of the new Fig. 4 in the manuscript:

Homogeneous freezing onsets of H_2SO_4/H_2O aerosol particles. The freezing onset conditions,T_{ice} and $S_{ice,fr}$, are displayed in comparison with the homogeneous freezing thresholds suggested by the WAC-based predictions by Koop et al. (2000) ~~(dashed and dotted black lines)~~ **(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).** ~~and the~~ **The used** water saturation pressures with respect to supercooled liquid water according to **MK2005** ~~Murphy and Koop (2005)~~ (solid black line) and ~~according to~~ **N2019** ~~Nachbar et al. (2019)~~ (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.

8. l. 341 and 350. The reason why the authors show 2 different fit parameters and procedures here is not clear. Would the authors please choose one, and remove the one you do not want your readers to use from the manuscript?

We decided to only keep the unconstraint fit, as this better represents our measurement data. We adjusted Fig. 6 and the related descriptions and discussions accordingly.

Description of Fig. 6:

Figure 6. New fit line for homogeneous freezing onsets of H_2SO_4/H_2O 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(Sice)

=a+1/T·b. The parameters are a=−1.40±0.05 and b= 390±10 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 Sice-T-space and compared to Koop2000 and the water saturation lines suggested by Murphy and Koop (2005) and Nachbar et al. (2019). ~~Panel (c) and (d): The fit shown in panel a is constrained to the well-known homogeneous freezing conditions of pure water at T= 235 K and Sice= 1.44765 according to the parameterizations of Murphy and Koop (2005). The fit parameters for the constrained fit (red line) are a=−0.75±0.04 and b= 263±8 K and the goodness of the fit is R^2= 0.92.~~

Description and discussion in Section “3. Results and Discussion”:

The coefficients of the fit shown in Fig. 6a are a = −1.40±0.05 and b = 390±10 K. This fit transferred into the S_{ice}-T-space and compared to Koop2000 and the water saturation lines is shown in 6b (~~grey~~ **red** line) with the range of fit uncertainty (~~grey~~ **red** shaded area). The goodness of fit is R^2= 0.92. ~~In a next step, this fit is constrained to the well-known homogeneous freezing temperature of pure water droplets, so that when applied to atmospheric models it matches the freezing point of pure water droplets (see Fig. 6c and d, red line). The fit was fixed to a temperature of 235 K and S_{ice}= 1.45, which is the point of water saturated conditions according to the parameterizations of Murphy and Koop (2005). This point corresponds to a nucleation rate coefficient of about J_V= 4.5·10^{10} $cm^{-3}s^{-1}$ according to the parameterization of Koop et al.(2000) for the nucleation rate coefficient in dependence on the temperature (T= 235 K) and water activity (a_w = 1 for pure water). This nucleation rate coefficient is in the range the AIDA experiments are sensitive to (J_V = 5·10^8 to 10^{13} $cm^{-3}s^{-1}$) (Möhler et al., 2003). The coefficients of the constrained fit are a = −0.75±0.04 and b = 263±8 K. The goodness of the fit is also R^2= 0.92.~~
~~We suggest to use the constraint fit with the coefficients a = −0.75±0.04 and b = 263±8 K(see Eq. 1 and 6c and d, red line) for use in atmospheric models.~~ **Applying** ~~T~~this **new freezing threshold for cloud formation processes in the atmosphere,** ~~would then result in a shift of~~ the homogeneous freezing onset in cirrus formation **would be shifted** to ice saturation ratios of about 2.0 at temperatures around 185 K. A higher homogeneous freezing onset may also contribute to explain high ice saturation ratios reported for low temperatures in the upper troposphere in some field studies (Jensen et al., 2005; Lawson et al., 2008; Krämer et al., 2009; Krämer et al., 2020).

Conclusions:

~~We suggest a new parameterization for the homogeneous freezing onset of H2SO4/H2O aerosol particles, which is based on~~ **A**~~a~~n empirical fit to the AIDA results with the form ln(S_{ice}) = a+ 1/T·b with fit parameters a = ~~−0.75±0.04~~ **−1.40±0.05** and b = ~~263±8~~ **390±10** K **describes the observed homogeneous freezing onsets of H_2SO_4/H_2O aerosol particles in the chamber**. **This fit line is based on direct measurements of the freezing onset conditions at simulated cirrus formation conditions and provides an isoline for homogeneous freezing of sulfuric acid aerosol particles for nucleation rate coefficients between 5·10^8 $cm^{-3}s^{-1}$ and 10^{13} $cm^{-3}s^{-1}$.** ~~This fit is constrained to the homogeneous freezing temperature of pure water at 235K and water saturated conditions at this temperature.~~

9. l. 350-351. It is not necessary to state the same parameters and errors twice in adjacent sentences. Please remove.

We removed a part of this sentence, as suggested (see changes in the manuscript given in the response to comment 8).

10. WAC freezing curves in figures. It is not clear that the freezing curves for constant J_V are correctly determined. In a later paper, Koop and Zobrist[11] altered the homogeneous freezing curve of Koop et al.[1] by an offset in Δa_w of 0.008. It appears this is not accounted for in this manuscript.

The homogeneous freezing curves resulting from the fit to the homogeneous freezing data of micrometer-sized droplets in Koop et al. (2000) yielded a Δa_w of about 0.305, which is stated to refer to a nucleation rate coefficient of $J_V = 10^{10}$ $cm^{-3}s^{-1}$. In the more recent paper of Koop and Zobrist (2009), this Δa_w is corrected to about 0.313, as they used the more recent parameterization of Murphy and Koop (2005) to calculate $a_{w,i}$. For calculating the WAC-based freezing curves in our manuscript, we used the parameterization of $J(\Delta a_w)$ given in Koop et al. (2000). As the correction in Koop and Zobrist (2009) is more recent, we corrected our resulting values of Δa_w by 0.008, as suggested.

We mentioned the application of the correction in “1. Introduction”, as follows:

Also shown are homogeneous freezing onset lines calculated according to Koop2000 for nucleation rate coefficients of $J_V = 10^{13}$ $cm^{-3}s^{-1}$ (Δa_w = 0.3**2**, dashed line) and $J_V = 5 \cdot 10^8$ $cm^{-3}s^{-1}$ (Δa_w = 0.3~~2~~, dotted line) (Möhler et al., 2003) **and corrected according to the revised version of the homogeneous freezing lines by Koop and Zobrist (2009).**

11. Figure 3. Why doesn't the activated fraction go to 1.0? I expect that homogeneous ice nucleation is so fast that all particles should turn to ice? Is there that much vapor depletion due to the first few ice crystals that form that the authors cannot nucleate all aqueous droplets?

Yes, we assume that is exactly the case. As one can see in Fig. 3 in the manuscript, the relative humidity decreases quickly after the ice onset, although we were still pumping. This shows that the water vapor depletion by the formation and growth of the first ice crystals is indeed very efficient. As the larger particles in the aerosol population have a higher freezing probability due to their larger volumes, they freeze first and the rapid depletion of the supersaturation in the gas phase prevents smaller aerosol particles from freezing.

12. Figure 4 and 6. There is a bit of a bias here (some systematic uncertainty that is not explained?) that the majority of ice saturation data points at temperatures warmer than 210 K are lower than homogeneous freezing estimates. Then, data is mostly higher than homogeneous freezing estimates when temperatures are colder than 210K. Would the authors care to comment on this somewhat systematic uncertainty? In addition, if there is

no theory or physical explanation to back up their measurements (see major comment), their data is more suspect to unknown experimental artifacts or errors.

In the AIDA chamber we have several temperature sensors distributed in the chamber volume. As explained in Section “2.4 Analysis of uncertainties”, the deviation between the measurements of the different sensors is usually below 0.1 K. During an expansion, this deviation increases and we have a wider temperature distribution inside the chamber. The freezing onset temperatures given in the manuscript are referring to the mean temperature calculated from the different sensors. Assuming that parts of the volume are colder than others and first ice formation is expected to occur in the coldest parts, the mean temperature might overestimate the actual freezing onset temperature. This uncertainty is considered in the calculation of error bars of the ice onsets, as explained in Section 2.4. Considering the upper limits of these error bars, the ice onsets agree with the homogeneous freezing onsets predicted by the WAC according to Koop et al., 2000.

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