

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

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.*<sup>1</sup>. However, their results deviate from Koop *et al.*<sup>1</sup> 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.*<sup>2</sup> instead of Murphy and Koop<sup>3</sup> 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<sup>1,4</sup>. In Koop<sup>4</sup>, 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 effects

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<sup>4</sup> 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.

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<sup>4</sup> claims a uncertainty up to 5% in temperature from the freezing line, which translates to an error close to  $\pm 15$  K in temperature and  $\pm 0.08$  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.
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<sup>5</sup> 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.*<sup>6</sup> 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<sup>4</sup>. When  $RH_i = 95\%$  and  $T = 185$  K, the weight percent of sulfuric acid solution in equilibrium is roughly 50%<sup>7-9</sup> 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<sup>4</sup>. 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.

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.*<sup>1</sup>, 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.

### Minor comments

1. l. 6. The WAC is not a function of aerosol particle size. Likewise, it is not a function of time either.
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.
3. l. 44-47. and 327-329. It was already stated by Koop<sup>4</sup> 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.
4. l. 46. What E-AIM model did the authors use? I suppose Model I<sup>7-9</sup>. Please check the correct references on the E-AIM website.
5. l. 50-51. I think there is a mistake here. Higher values of  $\Delta a_w$  should yield higher values of  $J_V$ .
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.*<sup>10</sup> that the highest  $RH_i$  for clear sky is about 150%. Krämer *et al.*<sup>10</sup> 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.*<sup>10</sup> 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.*<sup>10</sup>, 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.

7. l. 334-335. If the  $\Delta a_w$  values would be used together with Nachbar *et al.*<sup>2</sup> 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.
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?
9. l. 350-351. It is not necessary to state the same parameters and errors twice in adjacent sentences. Please remove.
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<sup>11</sup> altered the homogeneous freezing curve of Koop *et al.*<sup>1</sup> by an offset in  $\Delta a_w$  of 0.008. It appears this is not accounted for in this manuscript.
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?
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.

## References

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