Review of "New investigations on homogeneous ice nucleation: the effects of water activity and water saturation formulations" by M. Baumgartner et al.

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This paper revisits the homogeneous freezing of supercooled liquid aerosol droplets in the cirrus regime. It is motivated by recent observations at the AIDA chamber which apprently disagree with the canonical parameterization provided by Koop et al. (2000). Within Koop's paradigm, the present study examines the sensitivity of the homogeneous nucleation threshold and nucleated ice crystal number to changes in the expressions of liquid water saturation pressure and water activity in solutes.

The manuscript is generally well-written and I appreciate the authors' effort to detail the assumptions behind Koop's homogeneous freezing theory. Nevertheless, I find that major revisions are required before the paper can be considered for publication. I have reservations about part of the approach and several major points (see below) should be taken into account and corrected or clarified.

Major concern

In a few simulations, the aerosol equilibrium and nucleation rate calculations employ different, inconsistent formulas for water activity within the aqueous aerosol. This results in an inconsistency, which is acknowledged for example p 29 line 515. One of the inconsistent numerical experiments shows an improved agreement with AIDA ice onset observations (Fig. 15).

In my opinion, this inconsistency alters the original concept of Koop et al. (2000) which not only synthesizes earlier laboratory experiments but also aims at simplicity, taking advantage of thermodynamic constraints. Those include:

$$a_w^i = \frac{p_{i,sat}}{p_{sat}} \tag{1}$$

and Köhler theory for aqueous aerosols in equilibrium, namely:

$$a_w = S_i \, a_w^i \, \exp\left(\frac{-2\sigma}{R_v T \rho \, r}\right) = RH_w \, \exp\left(\frac{-2\sigma}{R_v T \rho \, r}\right) \tag{2}$$

In Equation 2, the resulting equilibrated water activity in the aerosol, a_w, depends on the analytical expression of water activity in the solution only through the factor r. If the curvature is neglected (i.e. if r is sufficiently large), Equation 2 reduces to the equilibrium formula proposed by Koop et al. (2000):

$$a_w = S_i \, a_w^i \tag{3}$$

in which aerosol water activity is set by environmental conditions only and is virtually independent of aerosol properties. As a consequence, the nucleation probability does not depend (or only marginally, through r) on the formula used for water activity in the solute. This is actually noticed (though not explained) by the authors: in consistent set-ups, they obtain similar nucleation thresholds although the formulas used for water activity are different (p 29 lines 518-519).

However, by employing inconsistent expressions for water activity between the aerosol equilibration (Köhler) and the freezing rate calculation, the authors artificially break the link between environmental conditions and the nucleation rate implied in Koop et al. (2000). Namely, instead of having the activity in the solute given by Eq. 3 (as an approximation to Eq. 2), it now follows :

$$a_w = f_{1\to 2}(S_i \, a_w^i, T) \tag{4}$$

where the function $f_{1\to 2}$ converts activity from formulation 1 ($a_{w,1}$ used in the Koehler routine) to formulation 2 ($a_{w,2}$ used in the nucleation rate computation) and is defined such that:

$$a_{w,2}(x(r), T) = f_{1\to 2}(a_{w,1}(x(r), T), T) \tag{5}$$

I believe this implicit replacement of Eq. 2 (or 3) by Eq. 4 (or a similar one with Kelvin correction) is the reason for the significant sensitivity of the nucleation thresholds to water activity formulations in the authors' simulations, not only in Sect. 4.3 but also in Sect. 4.4.

This important point needs to be accounted for and discussed early on by the authors. For clarity, I also would also ask them to drop the "most" when referring to the "most consistent" configurations, since they are "just" consistent. Note that this comment does not affect the conclusions regarding the impact of the formula used for water saturation.

Other comments

- I noticed differences between figures 6 and 8 at low vertical velocity where the small time step result exceeds that obtained with the large time step by a factor of about 2. This should be explained or corrected.
- Related to my main comment, I disagree with the authors regarding the impact of aerosol properties (in particular, aerosol radius r). At the beginning of the paper, it is argued (as in Koop et al., 2000; Kärcher and Lohmann, 2002) that the dependency on aerosol size is moderate, and cannot explain the differences between the AIDA chamber experiments and simulations based on the classical Koop approach.

Comparing Fig. 10 with Fig. 11 demonstrates that the impact of the aerosol size distribution, albeit present, remains limited.

Then, on several instances, the authors attribute changes in the nucleation threshold to changes in the aerosol radius r associated with Köhler equilibrium: Sect. 2.2, lines 446-460 (which seemingly contradict lines 446-460 where the primary importance of ice activity formulation is recognized) and Sect. 2.4, lines 526-546. As decribed in my main comment, I would guess that the apparent sensitivity to aerosol size is an artifact due to the inconsistent use of different solute water activity formulations.

- The paper rests solely on numerical investigations, whereas the authors have made valuable contributions to the theoretical analysis of homogeneous freezing of aqueous aerosols (e.g. Baumgartner and Spichtinger, 2019). Couldn't some of this analysis be useful here ? It would help explain and synthesize the results (such as the insensitivity of nucleated ice crystal number to the activity formulation).
- Why are the freezing onset simulations limited to the range 190-230 K? The relevant temperature range for cirrus extends down to ∼180-185 K (tropical tropopause layer) as do the experiments of Schneider et al. (2021).

Presentation

- The goal of the study is not entirely clear, is it (a) an evaluation paper for the nucleation scheme of CLaMS-ice, or (b) an investigation of the impact of water activity and saturation formulation on homogeneous freezing calculations (as suggested by the title and introduction)? If (b), I would encourage the authors to rephrase part of the text to emphasize that most conclusions apply in general and not only to their specific numerical model. They could remove/shorten some of the many references to the code (l 324, ...).
- The paper could be more concise. For instance, some figures and discussions could be moved to the appendix/ supplementary information. I am in particular referring to Fig 8 (p 18-19) which shows the sensitivity of the model results to the time step and illustrates that, for large vertical velocities, the calculations in Figs 6 and 7 had not converged. I would discuss this in an appendix and only keep figures 6 and 7 with the converged (i.e. 5 ms) time step. Also, some panels in Figs. 6-9 could be moved to the supplementary information, to limit the number of panels in the main body of the paper and make the relevant information more accessible.
- It would be useful to have a table or schematic summarizing where each parameterization/formula is used in the model for a given set of experiments (i.e. the water vapor saturation and water activity parameterizations).

Specific comments:

1. p 3 l 60: remove brackets

2. p 3 l 67: is this comment relevant in the introduction ? the point about latent heat release is not discussed further in the text and does not seem essential to me.
3. p 15 Sect 3.4: I would specify already here the aerosol characteristics and water saturation formula used by Kärcher and Lohmann (2002)
4. p 24 l 445: the Spichtinger et al. paper is not yet published. Putting a version on archive would be useful.
5. Fig 10, 11: the equation number of Koop activity is missing in the legend
6. p 29 l 518-519: This is expected I believe (see main comment).
7. p 29, Eq (21): The reference formula/value used for the surface tension σ should be specified.
8. p 32, lines 582-583: the authors can reproduce the nucleated number concentration "as long as the mean size and width of the size distribution of the aqueous solution particles from the AIDA experiments are known". How do they fit the dry aerosol radius to match the hydrated observed radius ? How strongly do the presented results depend on this fit? Furthermore, is the distribution of dry aerosols in the previous figures consistent with the aqueous aerosol in the AIDA experiments shown in Fig. 2 of Schneider et al. (2021) ($r \sim 250$ nm) ?
9. Fig. 15: If possible, error bars should be provided for the experimental values.

References

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