

## Review of „Analysis of isothermal and cooling rate dependent immersion freezing by a unifying stochastic ice nucleation model” by P. A. Alpert and D. A. Knopf

The manuscript introduces a parameterization of heterogeneous freezing processes which is based on Classical Nucleation Theory (CNT) and the use of a single contact angle, while allowing for a variation in surface area of the ice nucleating particles (INP) from droplet to droplet. The model is then used to reproduce a suite of different measurements from different groups, and also a sensitivity study is included.

The effect of variations in surface area certainly exists and has to be accounted for. However, I feel that this effect is presented much too pronounced in the present study and the tone of the whole manuscript has to be tuned down. Reasons for this are twofold: 1) The model introduced here only used a single contact angle, while it has been shown in the past, that this produces a much steeper temperature dependence of the ice nucleation process than is observed in experiments (e.g., Zobrist et al. (2007), Welti et al. (2012), Broadley et al. (2012), Augustin et al. (2013), to name only a few). This has been overcome by assuming a contact angle distribution. And while it is not yet known, on a basic level, how ice nucleating sites on INP look like, it is generally believed that they are not all the same in a single sample, particularly not when a mineral dust sample is used, as these usually contain more than one type of mineral. This makes the assumption of a single contact angle implausible. 2) Also, the width of the surface area distributions in the droplets in some of the experiments, as ascribed by the authors of the present study, seems to be much larger than seems reasonable based on the methods used in these experiments. This, together with the use of a log-normal distribution for the surface areas present in the different droplets, seems to overestimate the effect of the surface area variation. This shows in uncertainty ranges given for the different measurements that were modeled by the parameterization, which, in some cases, are excessively larger than the variation in the measurements themselves, with measured values appearing centered within the range.

As a further point, it seems that the manuscript becomes unnecessary long by mentioning the dependence on water activity (or relative humidity, RH) as represented in the model. The effect of variation in the surface area was discussed for immersion freezing measurements where measurements were done on diluted droplets, and therefore the occasional remarks or paragraphs dealing with concentrated solutions seems off the main track of the work presented here. This makes this already long paper even longer.

Therefore, the paper needs major revisions before it can be considered for publication in *Atmos. Chem. Phys.*. However, the topic as such is an interesting one, and when following the remarks given above and the more specific ones given below, a publication in this journal might be appropriate.

Sec. 2.1 and throughout the text:

When comparing your model results with data from literature, it is interesting to note that the ranges you calculate in many cases are much larger than the scatter of the data. This might indicate that you overestimate the variability in the ISA variation. You argue with a range of two orders of magnitude in droplet volumes when you derive  $\sigma$  for Wright and Petters (2013). Translation of that to a  $\sigma$  of 9.5 seems pretty much, though, and I would like to see a plot of the distributed ISA. (Typical atmospheric particle size distributions have modes where  $\sigma$  goes up to a maximum of roughly 2.) For other cold stage experiments, particularly when examined droplets all have the same size, the scatter in ISA should be much smaller. Indeed, you use smaller numbers there, but it remains unclear how

you derive values for  $\sigma$  in these cases. Additionally, values for  $\sigma$  you use for particles which are size selected with the Differential Mobility Analyzer (DMA) technique are beyond all plausible values, even when a shift or broadening due to the particle non-sphericity is taken into account (e.g., 8.2 for CFDC and LACIS (side note: there is a discrepancy as 8.2 is given in the text while Table 1 gives 7.7)). For spherical particles, a DMA typically has  $\sigma < 1.1$ . You have to use more reasonable numbers and justify these numbers much better.

Also, while a log-normal distribution might capture the distribution of INP surface areas in droplets when these droplets are prepared from suspensions (e.g., for cold-stage experiments), this is likely not the case for those experiments where particles were size selected using a DMA. This makes me wonder how your results would look like if you used a normal distribution, instead of a log-normal one, a topic you might want to address in your work.

p. 13113, line 9-13: You may note that the publications you list here are only some of a much larger number.

Paragraph starting at p. 13113: The list of publications you cite in lines 18-20 seems to mostly include studies for which the here mentioned parameters (T, RH, t and A) and their uncertainties are comparably well known. However, it seems to be said here that the respective values are difficult to determine, particularly in the cited publications. The text gives a misleading impression, and rewording is needed. Additionally, the sequence of models you cite is somewhat irregular. The DeMott-parameterizations aims exclusively at deriving INP concentrations, while others use CNT to model frozen fractions (a-pdf, active site, soccer ball model), and yet others omit a time dependence - but these do not appear grouped. This whole section could gain if it were reformulated.

p. 13114, line 3-5: Wex et al. (2014) used both, a time-dependent and a time-independent (i.e., such a simple) parameterization, including a freezing point depression, and both approaches described the measurements. It is therefore not correct that this cannot be done with these parameterizations.

p. 13114, line 17-18: Niedermeier et al. (2010) which you already cite above, belongs to this list given here, too.

p. 13114, line 25: You could give an estimate of the uncertainty in the surface area estimates already here, based on the literature you cite.

p. 13115, line 12-13: Why is it 7 independent studies but 8 different instruments? Please check.

p. 13115, line 25: Droplets "will" not necessarily possess different ISA, at least not to the extent you suggest here, so exchanging "will" by "might" is more appropriate.

p. 13116, line 8-14: You are correct that it is often assumed that all droplets contain the same ISA. But I am not convinced that this is necessary in principle. As long as the total available ISA is known, derived parameters as e.g. surface site density, should be the same, no matter if all droplets contain the same ISA or if it is distributed. Otherwise experiments with poly-disperse INP, as e.g. done in AIDA, should result in clearly different surface site densities, when compared with methods which constrain the ISA per droplet to a much narrower range. This, however, is not what is seen in the comparison given in Hiranuma et al. (2015).

And although it is usually not done, it is not true that ISA variability can generally not be resolved from experiments.

p. 13118, line 8-12: The wording here seems to suggest that the ABIFM is particular in that it gives parameterizations for  $J_{het}(T)$ , which is not the case (see e.g., some of the literature you cite yourself). Please tune this down.

p. 13120, line 12: To avoid confusion, start this sentence with "Two of these test cases, Iso1 and Iso2, have uniform ISA ... "

p. 13121, line 3-15: Yes, in your case, the deviation from a log-linear relationship originates in the assumption of a log-normally distributed ISA, where some droplets will have large ISA. The same behavior (i.e., a divergence from a log-linear relationship) was observed already in Niedermeier et al, (2011), only there a variation in the contact angles ascribed to the different particles caused the effect. It will certainly be difficult to determine how much of the observed shape of a curve is due to the existence of a distribution of contact angles or of ISA, but to be complete it has to be discussed here, that not only an ISA distribution causes the observed behavior.

What do you want to say with the last sentence in this paragraph? This is not clear to me, please consider rewording or removing it.

p. 13121, line 26: Here and in other cases, when you use nucleation rate coefficient in your calculations, I would have preferred to get the information about the origin of these numbers much clearer. The information can sometimes be found in the text, but often only much later than I would have preferred it. Please edit the text accordingly.

p. 13122, line 19: You base the calculation of the surface area on a gas adsorption method (BET), which, however, is only one way to determine the surface area. You might want to stress the fact that surface area is not an unambiguous parameter.

p. 13124, line 5-7: Same as said above wrt. p. 13121, line 26: I will not list all of the occurrences, but here again it is not clear to me where the nucleation rate coefficient came from.

p. 13124, line 16-18: You mix two things, here: The large uncertainty from the small number of droplets which is examined which you get from your calculation is not related to the different ISA per droplet. The latter depends on how uniformly the experimenter manages to produce the droplets.

p. 13125, line 6-7: Values for nucleation rate coefficients for K-feldspar (microcline) were given in the supplement of Augustin-Bauditz et al. (2014).

p. 13125, line 19-20: As mentioned before, the use of a contact angle distribution does a similar job, so this sentence cannot be kept as it is now.

p. 13125, line 28 to p. 13126, line 2: The approach used here also uses an empirical parameterization of some kind by assuming large variations in ISA, and as such is not better or worse than other comparable models. Please reformulate.

Sec. 3.2: The method comparing apparent and actual values is nice, however, the conclusions again suffer from the fact that the principal assumption was that of only one contact angle (i.e., one nucleation rate coefficient) being present. This all has to be reformulated / thinned out respectively.

p. 13129, line 15-16: This goes along the line of my former remark: This new parameterization for a nucleation rate coefficient for feldspar would only be valid if the same ISA variability was used with it. Hence it might be advantageous to not deliver new parameterizations but to describe the effect of ISA variability and its magnitude, all on its own, instead.

p. 13131, lines 17-23: Again, and I know I repeat myself: this could only be said so clearly if your assumption of a single contact angle per substance were correct. This whole passage has to be toned down a lot.

p. 13132, line 5: "is not observed unlike" - double negative, always makes comprehension difficult.

p. 13133, line 7-8: The comparison done between  $J_{het}$  derived in Wex et al. (2014) and in Murray et al. (2011) and Pinti et al. (2012) is not viable. The differences in the derivation of the surface area (BET versus assumption of spherical particles) would need to be accounted for. But even more important, the comparison as done here compares two different kaolinites, data for Fluka-kaolinite from Wex et al. (2014) and for CMS-kaolinite, which is known to be less ice active, as used in the other two publications. Wex et al. (2014) did also include CMS-kaolinite, but the data from that publication you used here is that from Fluka-kaolinite. Accordingly, the mentioning of Fig. 7b on p. 13134, line 17 as an example needs to be removed.

p. 13113, line 21: Wex et al. (2014) also similarly used the time-independent approach (surface site density) and reports that this works almost as well as the time-dependent approach. Therefore this study does not clearly support the necessity of a time-dependent and stochastic treatment of the immersion freezing process.

p. 13135, line 3-4: The model simulations indeed fit the AIDA data, but a straight line representing  $J_{het}$  (the red line you drew) or likely even a time-independent approach would reproduce the data similarly well, so I do not see how this further supports the necessity of the quantification of the ISA variability.

p. 13135, line 10-18: The singular approach is meant to represent averages, so it is correct to say that it cannot capture an increase in scatter in the data due to stochastic effects. But although indeed Fig. 8b shows an increase in scatter as  $T$  increases, it does generally not seem to be the case that the scattered data-points in Fig. 8A are captured within the limits of the model. Certainly here, and for other experiments, too, there are measurement uncertainties which are not captured neither by the singular approach, but also nor by your model. This might be worth pointing out, here.

p. 13136, line 2, and also p. 13139, line 20 and p. 13140, line 6 and possibly other occurrences: When referring to “stochastic uncertainty” here, what exactly do you mean, besides the influence of time, which is mentioned additionally in some occasions?

p. 13139, line 23: In some experiments / some methods, more than 1000 droplets are examined.

p. 13141, line 1: Using a concentration of illite particles of  $10^5/L$  is extraordinarily large and likely not representative for the atmosphere.

p. 13141, line 12 ff: MPC2 produces ice nucleation at higher temperatures, but not necessarily because of the total variability in ISA that you introduced, but because the droplet with the “best” INP will induce the freezing. In your case these are those droplets which have the largest ISA ascribed, and as the spread in the ISA distribution is large ( $\sigma$  of 5!), you find this shift by 5K. Also, when you then start to discuss Arctic conditions, it surely becomes unrealistic to assume a single substance. For atmospheric conditions, the heterogeneity of types of INP can be assumed to play a large role (i.e., the occurrence of different nucleation rate coefficients has to be expected). But in the way you treat it, you cover this heterogeneity with an unrealistic large spread in ISA.

p. 13145, line 2-3: This is already done in the work by DeMott et al. (2010) and DeMott et al. (2015), which you might mention here.

Rigg et al. (2013) is missing in the literature-list.

Table 1: Again a repetition, but it really needs to be made clearer in the text, where these values you use here come from, particularly  $\sigma$  and nucleation rate coefficients.

Literature (almost all of that was cited by you already, and I mainly include it here for completeness):

Augustin et al. (2013): Immersion freezing of birch pollen washing water, *Atmos. Chem. Phys.*, 13, 10989–11003, doi:10.5194/acp-13-10989-2013.

Augustin-Bauditz et al. (2014): The immersion mode ice nucleation behavior of mineral dusts: A comparison of different pure and surface modified dusts *Geophys. Res. Lett.*, 41, doi:10.1002/2014GL061317.

Broadley et al. (2012): Immersion mode heterogeneous ice nucleation by an illite rich powder representative of atmospheric mineral dust, *Atmos. Chem. Phys.*, 12(1), 287-307, doi:10.5194/acp-12-287-2012.

DeMott et al. (2010): Predicting global atmospheric ice nuclei distributions and their impact on climate, *Proc. Natl. Acad. Sci. USA*, 107(25), 11217-11222, doi:10.1073/pnas.0910818107.

DeMott et al. (2015): Integrating laboratory and field data to quantify the immersion freezing ice nucleation activity of mineral dust particles, *Atmos. Chem. Phys.*, 15(1), 393-409, doi:10.5194/acp-15-393-2015.

Hiranuma, N., et al. (2015): A comprehensive laboratory study on the immersion freezing behavior of illite NX particles: a comparison of seventeen ice nucleation measurement techniques, *Atmos. Chem. Phys.*, 15, 2489–2518, doi:10.5194/acp-15-2489-2015.

Murray et al. (2011): Heterogeneous freezing of water droplets containing kaolinite particles, *Atmos. Chem. Phys.*, 11, 4191–4207, doi:10.5194/acp-11-4191-2011.

Niedermeier et al. (2010): Heterogeneous freezing of droplets with immersed mineral dust particles – measurements and parameterization, *Atmos. Chem. Phys.*, 10, 3601–3614, doi:10.5194/acp-10-3601-2010.

Niedermeier et al. (2011): Heterogeneous ice nucleation: exploring the transition from stochastic to singular freezing behavior, *Atmos. Chem. Phys.*, 11, 8767-8775, doi:10.5194/acp-11-8767-2011.

Pinti et al. (2012): Ice nucleation efficiency of clay minerals in the immersion mode, *Atmos. Chem. Phys.*, 12, 5859-5878.

Welti et al. (2012): Time dependence of immersion freezing: An experimental study on size selected kaolinite particles, *Atmos. Chem. Phys.*, 12(20), 9893-9907, doi:10.5194/acp-12-9893-2012.

Wex et al. (2014): Kaolinite particles as ice nuclei: learning from the use of different kaolinite samples and different coatings, *Atmos. Chem. Phys.*, 14, 5529-5546, doi:10.5194/acp-14-5529-2014.

Wright, T. P., and M. D. Petters (2013): The role of time in heterogeneous freezing nucleation, *J. Geophys. Res.-Atmos.*, 118(9), 3731-3743, doi:10.1002/jgrd.50365.

Zobrist et al. (2007): Heterogeneous ice nucleation rate coefficient of water droplets coated by a nonadecanol monolayer, *J. Phys. Chem. C*, 111(5), 2149-2155, doi:10.1021/jp066080w.