

2nd round of reviews for “Analysis of isothermal and cooling rate dependent immersion freezing by a unifying stochastic ice nucleation model” by P. A. Alpert and D. A. Knopf, submitted to ACPD

As in my first review, I am still of the opinion that the topic dealt with in this manuscript is an important one and merits publication. But, also as in my first review, I feel that the manuscript currently still is not in such a shape that it can be published, and quite a number of further changes, additional explanations and corrections are needed. Also, I am somewhat disappointed at the fact that quite a number of my concerns, even major ones, were merely swept aside. (And it seems, based on the common answer to all reviewers that this was also done with concern from the other reviewers.) Considering this, I would understand if the editor decided to reject the manuscript.

My main points of criticism are still in the same ballpark as they were in the first round and are given below. I apologize if I repeat myself, but it seems the authors did omit some hints too easily, hence I feel I need to make some points clearly and maybe more than once.

My main concerns in short for the editor:

- the choice of a log-normal ISA distribution (i.e., the distribution of surface areas) might already be prone to overestimate conditions found in experiments and nature, particularly as often (and unjustified) very broad distributions were used
- the ISA distribution for the temperature dependent examples (IsoCFDC and IsoLACIS) were grossly overestimated
- moreover, for these two examples, it seems that a distribution of ISA is not even necessary to explain the measurements, and in fact there seems a change in efficient contact angle implicitly included even in J_{het} from the ABIFM, contradicting some of the statements made in the text. In fact, size segregated measurements should be good examples of cases where ISA variability only plays a small role, and I even interpret what I see in the current manuscript to show that. In that respect, I would want to see an example in the manuscript which is similar to Cr1 and Cr2, but where the data pool created for further evaluation is based on a monodisperse IN population (the way the examples Cr1 and Cr2 are made and interpreted now, circular reasoning is at work - and opposite effects are to be expected when it is done the way I suggest it here)
- altogether, the manuscript is VERY long, and I question if all of it is really needed; one possible solution would be to remove the following examples: IsoBR, IsoHE1, IsoHE2, IsoDI1-3, IsoCFDC, IsoLACIS, CrHE1, CrHE2, CrDi1, CrDi2, CrNI1 and CrNI2. I know that this means to remove almost all connection to literature data, and I only suggest that as these examples are often not treated correctly (see e.g., the very large width of the ISA distribution and the way of deriving the ISA variability for IsoCFDC and IsoLACIS). If they remain, values assigned to the parameters have to be discussed and justified better, some of them have to change.

Here now my comments in more detail:

While it is easier now to trace the origin of some of the parameters used for the simulations (for a few open questions see “Technical comments”), this also reveals inconsistencies more clearly. The largest one still enclosed the choices made for σ_g . It is VERY disappointing, that nothing in this regard was changed compared to the first version. Also, by now I have to tell you that it is mandatory that you show the ISA distribution in a separate figure (using a log-scale on the y-axis!) if you want to

show the respective examples (IsoBR down to Iso LACIS and CrHE1 down to CrNI2). The width of the ISA distribution is the key parameter in your work, but values you assign to it are mostly not justified.

The example IsoWR is one for which the origin of the parameters used for the simulations are all well explained, and particularly also the derivation of σ_g is comprehensible. In the following, however, the impression arises that σ_g is merely used as a fit factor to make the simulations fit the measured values. Here is why I got this impression:

- While IsoHe1 has a comparably small σ_g of 2.2 (compared to other values you've used), it is much larger for IsoHe2 (8.5). Where does the discrepancy come from, or in other words: Why did you choose the respective values?

- This large σ_g used for IsoHE2 is particularly puzzling, as Herbert et al. (2014) are even cited to have "dispensed [droplets] with a digital micropipet with high accuracy, ...". How can σ_g then be almost as large for IsoHE2 (8.5) as it was for IsoWR (9.5), where for the latter the droplet generation was such that the droplet diameter alone varied from 50 to 250 micrometer, and the variation in ISA was assumed to respectively cover 2 orders of magnitude? IsoHE2 therefore should have a MUCH lower σ_g .

- On the other hand, it is said that (p. 13, line 413-415): "It can be expected that σ_g is the same for all three simulations, due to the fact that Diehl et al. (2014) likely used identical bulk water-illite solution stock." Why then do the values for σ_g for the different simulations for IsoDI1-3 vary from 4.2 to 9.1 and 1.5? This is unjustifiable, and again, covers a large range of variability, much larger than I would expect based on your remark I cited here.

On top of that, also the selection of J_{het} is not explained well. Even after having read particularly Section 2.2.2 several times, I still get the impression that the values for J_{het} you derive for the simulations are based on ABIFM. However, later in the text you often compare the values you used to those obtained with the ABIFM, which then makes no sense. If the values you use for the simulations are NOT derived using the ABIFM, then where do they come from? Concerning this, also see my "Technical comments". This also was one of my concerns in the first round of review, and it was not improved satisfactorily (and I've spent more than a full working week with the manuscript up to now, so it is not that I am going over it hastily).

page 7, section 2.2.1: I do not see how this section contributes much to the topic of the manuscript. Again, this is something I remarked in the first round already. All simulations you do concern immersion freezing, hence there is no freezing point depression, and it is somewhat confusing having to learn how J_{het} depends on water activity (which is not needed anywhere), while no clear statement is made about the dependency of J_{het} on temperature (which would actually be important, as you also model experiments for which T was varied). Looking at your own work (Knopf & Alpert 2013), I assume, based on the good comparisons between the output of the ABIFM and literature data, that the ABIFM- $J_{het}(T)$ -values generally follow the course with temperature which is observed in experiments. This seems to be corroborated when looking at Fig. 7 B and will become important in my arguments later.

On page 9, line 296-297, you state the following: "From this we can conclude that the effects of droplet numbers and ISA variability on f_{ufz} can be decoupled and independently assessed." This is in

contradiction to several statements you give later on (particularly on page 12, but not only there), where the impression is made that σ_g cannot be determined well enough due to the low number of droplets examined in the respective experiments. You even say explicitly: "To better constrain σ_g , more stochastic certainty is required by application of more droplets or conducting multiple experiments." You have to remove this inconsistency, i.e., the sentence on page 9 and related statements have to be removed.

On page 12, line 389-391, you still state: "Herbert et al. (2014) assumed that each droplet possessed the same ISA, however, this assumption is not supported due to the large stochastic uncertainty from the small number of applied droplets." - The fact that only a small number of droplets was examined does NOT imply, that ISA varies largely between them! This, however, is how I understand this sentence. Rather, as you quite correctly state on several occasions, a comparably large scatter could occur due to the low number of droplets examined, and NOT NECESSARILY due to a variation in ISA. I remarked on that statement before, and the change you did to the sentence prior to the one I cite here did not improve this part of the paper sufficiently. Remove this statement.

On page 12, line 391-394, you state: "The ABIFM yields $J_{\text{het}} = 1.75 \times 10^{-2} \text{ cm}^{-2} \text{ s}^{-1}$ at $T = 255.15 \text{ K}$ and $a_w = 1.0$ which is within an order of magnitude of J_{het} used in IsoHE1." Why is J_{het} used in IsoHE1 different by one order of magnitude? Where does this deviation come from, i.e., how was the value used in IsoHE1 chosen? Again, more related questions in "Technical comments".

On page 11, line 352-354, you state: "This implies that the droplet to droplet variability in ice nucleation efficiency parameterized by a contact angle or active site distribution is potentially unimportant." This cannot be said here, based on the evidence you only showed in your manuscript up to this point. And as I will try to elaborate in the following, it cannot be said at all.

Up to that point in the manuscript, you only did look at the time evolution of the ice nucleation at a single temperature. And while the observed freezing behavior might be explicable when using a single value of J_{het} together with a (still wide, maybe too wide) distribution of surface areas (which, in fact, you did show here), this cannot generally be expanded to the ice nucleation occurring over a wide range of temperatures.

Considering a wide range of temperatures, it has been shown in literature that a single J_{het} (which is similar to the use of a single contact angle) cannot explain the slope that has been observed for data on ice nucleation versus temperature (e.g., Broadley et al., 2012; Welti et al., 2012; Augustin et al., 2013; Niedermeier et al., 2015). And for most of these publications, size segregated particles were used - and below I show that they are MUCH better constrained in size than you suggest. In short: For the studies on size segregated particles (IsoCFDC and IsoLACIS) you replaced σ_g by choosing an approach using the multiple charge distribution, which, however, you did in such a way, that it will (again) result in a too broad distribution of surface areas (as said, I will go into that in detail below). But even then: isn't it that the broad distribution only creates the shaded areas in Fig. 7, while $J_{\text{het}}(T)$ from measurements already fit to the red line in Fig. 7 B (i.e., ABIFM-results with no ISA variation).

The first version of your manuscript made me, and (as I take from your response to all of us) obviously also the other reviewers believe, that you only use a single contact angle approach. This is, after all, what you stress and what seems to be important to you. However, values of J_{het} used for simulations in IsoCFDC and IsoLACIS are simply given by you as "calculated ... based on ABIFM".

Above I already said that I assume that “ABIFM- $J_{\text{het}}(T)$ -values generally follow the course with temperature which is observed in experiments.” In fact, the red line denoting the ABIFM- $J_{\text{het}}(T)$ -values in Fig. 7 is similar to the one for $J_{\text{het}}(T)$ shown in Wex et al. (2014) (their Fig. 3). Again, and I go in circles, e.g., Broadley et al. (2012), Welti et al. (2012), Augustin et al. (2013) and Niedermeier et al. (2015) all showed that a distribution of contact angles is usually needed to describe the course of the temperature dependency of J_{het} (even for such a substance containing ice nucleating macro-molecules (see Augustin et al., 2013), which should vary less from molecule to molecule than ice active sites in a mineral dust sample which typically always also includes a variety of minerals). While you might argue that Broadley et al. (2012) suffered from a broad ISA distribution, this is not the case for the other three (see below on multiple charge distribution).

In summary: it is safe to say that $J_{\text{het}}(T)$ as obtained from the ABIFM already implicitly includes different contact angles. If it didn't, it would feature a much steeper increase (it is easiest to be seen in Fig. 1 in Niedermeier et al., 2015, but again you can also additionally refer to Braodley et al., 2012; Welti et al., 2012; Augustin et al., 2013). And therefore, even your own analysis includes the variation that you potentially deem unimportant. Hence, the statement from your paper on page 11, line 352-354 has to be removed!

page 14, line 474ff: Above, you say that the input into creating your data base which mimicked the experiment, “variable ISA per droplet is applied and used to calculate $P_{j,\text{frz}}$...”. Here now you claim that “These significant differences do not support the null hypothesis and imply that when experimentally deriving J_{het} , the assumption that ISA per droplet is identical is invalid.” This sentence needs to be amended such that it becomes clear that this is indeed true when a broad ISA distribution is present (as it was, because this is what you used to create your data pool with; with “data pool”, I mean your “freezing record [which] is treated as a freezing data set”), but that this will not be the case when the data pool is created with droplets which really all have the same ISA! BTW: the latter case has to be added to your publication, i.e., create a data pool for which you used monodisperse IN, i.e., no variation in ISA, and do the same analysis, once assuming a really wide ISA distribution, once no variation in ISA. This will show that if the experimenter really manages to create a narrow ISA distribution, it is justified to omit the respective effect, and the remaining observed effects than can be examined wrt. changes in contact angle or other effects.

Furthermore, you say that “Figure 4b shows that accounting for variable ISA, $J_{\text{het}}^{\text{actual}}$ for Cr1 and Cr2 is consistent and in very good agreement with model input J_{het} (red curve).” This again has to be the case - you retrieve what you used as input! This is circular reasoning and cannot be used to show anything besides the fact that when there indeed is a broad ISA distribution, this has to be accounted for. The text has to be rewritten respectively.

Similarly, there is no absolute need to assume that the dependency of $J_{\text{het}}^{\text{apparent}}$ on temperature is truly that of the red line (e.g., Figure 5 B) (BTW: it is somewhat annoying that I have to blow up this and other figures to 300% before I can start to read the script - just increase the figure size next time). The red line is what you obtain when you assume a broad ISA distribution, and which you find again (Figure 5 C). But the temperature dependency could as well be the one shown by the data-points in Fig. 5 B. This again proves nothing, particularly as σ_g in this case is unreasonably large (see my respective comment above).

page 18, line 590ff:

As for the use of a multiple charge distribution, this is a valid first step towards determining the extent of variation in surface areas, but not the full story. Therefore, you grossly overestimate the number of multiply charged particles.

First, the distribution is a discrete one, i.e., multiply charged particles appear AT certain sizes, and not in between, as you suggest with the distribution you fitted (for 300nm singly charged particles, they appear AT ~500nm, and AT ~700nm, ...). Then it depends on the way a DMA (Differential Mobility Analyzer) is operated (particularly ratio of flow to sheath air), how broad the distribution around these discrete sizes is, and it certainly will not be broad enough to justify the kind of distribution you fitted to the data-points in Figure S1.

Next, and most important, the multiple charge distribution you used can be interpreted as similar to the probability that a particle of that particular size carries the respective number of charges. Hence, this discrete distribution then has to be merged with the total size distribution entering the DMA. Every researcher who has experience with a DMA will strive to generate the aerosol in such a way that the selected size is larger than the median size of the total size distribution. In that respect, already Lüönd et al. (2010) said: "For sizes well above the median size of the total size distribution, the contribution of multiple charges is negligible." Concerning multiple charges Wex et al. (2014) state: "We wanted to examine size-selected particles, and to facilitate the size selection a rough pre-selection was done; i.e., particles with aerodynamic diameters above 560 or 1000 nm (for the generation of 300 or 700 nm particles, respectively) were separated with a MOUDI impactor." Therefore it can be well expected that, besides maybe some doubly charged particles (~500nm), multiply charged particles of larger sizes will not play a role in data for 300nm particles from Wex et al. (2014). And even though the doubly charged particles likely are present to some extent, their fraction is below the one suggested by the mere multiple charge distribution (where 500 and 300 nm particles appear with ~0.5 / ~2.4, taken from your Figure S1, i.e., the fraction of 500nm particles is below 20%).

Admittedly, the total size distributions are generally not reported, nor the size distributions of the particles after size selection, so it will be impossible to determine the true fraction of multiply charged particles. But the method you used overestimates that number grossly (see the 20% I estimated as the maximum fraction of doubly charged particles).

Moreover, I understand $J_{\text{het}}^{\text{apparent}}$ to be the parameter for which no variation in ISA was assumed, and this clearly covers all measured datapoints already fully.

This brings me back to a point I had earlier. The manuscript contains the following sentence (p. 18, line 596ff): "We find agreement between $J_{\text{het}}^{\text{apparent}}$ and data by Wex et al. (2014) when accounting for multiple particle charges predicted by Wiedensohler and Fissan (1988)." This is confusing in the first place, as "apparent" denotes these cases when "a monodisperse IN population [is assumed]" (p. 13, line 443). So you might have meant "actual" here, instead of "apparent"? But the first part of your sentence actually is true: "apparent" fits well to the data, hence the multiple charge distribution does not need to be accounted for. In Fig. 7 B, both $J_{\text{het}}^{\text{apparent}}$ and actually also the red line alone (ABIFM Fluka Kaolinite) fits the data quite well, even without any broadening. To me this indicates that already $J_{\text{het}}(T)$ in the ABIFM suffices to model the data, without any variations in the surface areas. And to this end, I argued above that this includes a changing effective contact angle!

Hence a sentence I criticized earlier (line 352-354: "This implies that the droplet to droplet variability in ice nucleation efficiency parameterized by a contact angle or active site distribution is potentially unimportant.") cannot be stated. Remove it! And all related statements throughout the manuscript!

Technical comments:

p. 4, line 97-99: "For example, Rigg et al. (2013) showed that the single contact angle model, a-PDF model, active site model and singular description cannot describe the freezing point depression." This sentence is somewhat unfair, as these models were never made to describe a freezing point depression. It is also unnecessary, as your current manuscript does not really deal with concentrated droplets where a freezing point depression could occur. Remove!

p. 4, line 102: Delete the ". surface."

p. 4, line 105: Again: Wex et al. (2014) used both, a singular description and a time dependent one. In fact, what you refer to here was only mentioned in the appendix. Correct the sentence accordingly.

p. 12, line 375: Add "was chosen" behind "... = 8.3"

p. 12, line 376-377: "... is in excellent agreement with model derived J_{het} ..." - explain what you mean by "model derived J_{het} "

p. 12, line 381-382: "parameter $A_g = 1.2\text{cm}^2$, in good agreement with experimentally derived $A_g = 2.4\text{cm}^2$, ..." - how was A_g experimentally derived, by whom?

p. 12, line 382 and Table 1 give $A_g = 1.2\text{cm}^2$, while on p. 12, line 399, it is said "similar to $A_g = 2.0 * 10^{-2}\text{cm}^2$ used in IsoHE1." - Also, the value you claim to have used for IsoHE2 in the text is given with $1.85 * 10^{-2}\text{cm}^2$, while it is $2.0 * 10^{-2}\text{cm}^2$ in Table 1. Check this, something is wrong here. Also: why is A_g seemingly two orders of magnitude different for IsoHE1 and IsoHE2 (judging from the values in Table 1)?

p. 17, line 569: Sorry, this seems to have slipped my attention in the first round. The following sentence is not correct for LACIS: "It is important to note that for both instruments, droplet freezing is not observed and instead, the number of ice crystals is optically detected." Instead, detection of freezing at LACIS is described in Wex et al. (2014) as follows: "At the LACIS outlet, a self-built optical particle spectrometer (TOPS-Ice; Clauss et al., 2013) determines if the arriving hydrometeors are liquid droplets or frozen ice crystals, resulting in the determination of a frozen fraction, f_{ice} , i.e., the number of frozen droplets divided by the total number of liquid and frozen droplets." Remove the sentence given here and the following one!

Literature:

Augustin, S., H. Wex, D. Niedermeier, B. Pummer, H. Grothe, S. Hartmann, L. Tomsche, T. Clauss, J. Voigtländer, K. Ignatius, and F. Stratmann (2013), Immersion freezing of birch pollen washing water, *Atmos. Chem. Phys.*, *13*, 10989–11003, doi:10.5194/acp-13-10989-2013.

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Herbert, R. J., B. J. Murray, T. F. Whale, S. J. Dobbie, and J. D. Atkinson (2014), Representing time-dependent freezing behaviour in immersion mode ice nucleation, *Atmos. Chem. Phys.*, *14*(16), 8501-8520, doi:10.5194/acp-14-8501-2014.

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Rigg, Y. J., P. A. Alpert, and D. A. Knopf (2013), Immersion freezing of water and aqueous ammonium sulfate droplets initiated by humic-like substances as a function of water activity, *Atmos. Chem. Phys.*, *13*(13), 6603-6622, doi:10.5194/acp-13-6603-2013.

Welti, A., F. Lueoend, Z. A. Kanji, O. Stetzer, and U. Lohmann (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, H., P. J. DeMott, Y. Tobo, S. Hartmann, M. Rösch, T. Clauss, L. Tomsche, D. Niedermeier, and F. Stratmann (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.