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Discussions

Interactive comment on "Using critical area analysis to deconvolute internal and external particle variability in heterogeneous ice nucleation" *by* Hassan Beydoun and Ryan C. Sullivan

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This manuscript presents a new mathematical approach to describe laboratory immersion freezing data based on the concept of ice active surface sites in combination with a stochastic model of heterogeneous freezing. The unique feature of this approach is that it assumes a continuous distribution of the ice nucleating activity, expressed as a function of contact angle, θ, of a particle's surface without defining the size or number of active sites. This yields a function, g(θ), to determine the freezing probability for an ice nucleating particle. This approach is applied to examine the internal and external variability in immersion freezing experiments which, in part, may be due to different particle concentrations among droplets. The authors derive a critical surface

area threshold. Above this threshold, active sites number densities, n_s, calculated from modeled freezing could be successfully applied to describe data. However, immersion freezing experiments conducted below this area threshold translate to higher n_s values compared to the commonly applied analysis. Adequate representation of frozen fraction curves using below threshold particle surface areas could be derived by subsampling θ. From this exercise, it is concluded that individual illite dust particles do not contain the entire range of ice active sites.

The topic of this manuscript fits well within the scope of ACP having published numerous ice nucleation experiments and parameterizations on this topic. However, I feel major revisions are necessary before this manuscript can be publsihed. Here follows a few general issues pertaining the presented work followed by more specific comments.

The manuscript is rather long for its content, very "wordy", and many sections are difficult to understand. Also, the writing in places is too sloppy, meaning superficial or stating generalizations without references or convincing proof. I strongly suggest to carefully revise the text and shorten some sections but others may need more information to be better understood as indicated below. For example, section 3.6 on time dependence is very confusing and the mathematical procedure is not clear.

This manuscript presents an attempt to describe immersion freezing data using a mathematical construct, i.e. by fitting experimentally frozen fraction curves. As stated in earlier works upfront, such as Niedermeier et al. (2010), an active sites concept is not based on a physical foundation or theory. Neither, is the effect of external and internal variability of active sites proven to be a physical concept. The Murray group implied this from fits to data. The scientific value of such (previous and this) approaches will be shown in time. I do not mind this mathematical exercise to somehow describe the experimental data in the lack of a physical model, however, these caveats and assumptions should be stated clearly upfront and the tone of the manuscript changed accordingly. In particular the last third part of the manuscript has to reworded since it reads as if all the results, effects, distributions refer to something "real" or "physical", which it does not in absence of a physical model. More careful language would be more appropriate.

As for the mathematical concept: A distribution referred to as a “g-distribution” is introduced. It is not clear of which kind, but always seems to be a normal distribution function. In principle, this concept is very much the same as the α-PDF, the updated soccer ball model (SBM) or other distribution based fits. The emphasis on continuous distribution values is not clear to me as both α-PDF and the SBM are continuous in a mathematically sense.

As the frozen fractions curves shift to lower temperatures due to a decrease in surface area and below the critical threshold area as stated here, g cannot reproduce the data. However, freezing data can be described when choosing contact angles and calculating g values as many times as necessary. The authors are correct that a new distribution for below threshold surface areas is not necessary. (If it were, would it imply that the fit is truly unphysical, i.e. not representing particle properties?) But obviously, drawing as many times as necessary from g (which contains all possible contact angle values) to represent the freezing curve does not mean anything physically. One could argue that the number of draws represent just another free “fit parameter”. In general, I am not surprised that data can be fitted with this mathematical construct, but the manuscript must include, state, discuss properly its assumptions. The emphasis to have discovered something “real” in view of these assumptions is incorrect. The effects may all be a result of an assumption that is not known to be true or even applicable. More studies and experiments are necessary.

I remain confused about the details of the method. It would also be beneficial to show g and the numbers of draws for different experimental data sets to establish this method. Many other questions remain and I mention a few here. It is stated that θ is randomly chosen but does this mean that θ is first sampled from a uniform probability density function, and then g(θ) is calculated? Does this method of draws also work equally well for above the surface area threshold? Is it correct to say that the g-distribution is not

a probability density function from which θ is derived and used in the J_het equation, but is it a scaling function or a change from a surface to line integral as stated in the manuscript?

The manuscript does not sufficiently discuss previous work on immersion freezing. On the model side, the authors could test if “subsampling” of an α-PDF or other distributions (deterministic etc., see e.g. Marcolli or Lohmann group) will result also in a better representation when surface area is changing – likely yes, if sufficient draws are allowed. The water activity based immersion freezing model by the Knopf group also can describe immersion freezing for illite. As far as I recall they do not need to invoke external or internal mixtures to consolidate freezing data obtained from differently sized particles.

Regarding experimental studies. Somehow it feels irritating that the authors, claiming to have a new parameterization model, just discuss one study by Broadley et al. and do not test their model with other studies. Also, some statements in this regard are not entirely correct. There are cold stage experiments that apply micrometer-sized droplets with rather uniform INP immersed within those droplets like the studies by the Koop and Knopf groups that include surface area and time variance. There is also CFDC data covering size and time dependence that could be tested by this new model. A “negative experiment” would also be beneficial, e.g. testing if frozen fraction curves from experiments employing smaller surface area result in a g distribution that cannot describe smaller or larger surface area freezing data. I believe the Pinti et al. freezing data would represent an ideal test case for this model and in fact, may be in contrast to the results here. Pinti et al. found that at large surface areas for a variety of dust particles, a unique freezing temperature of some droplets was observed warmer than the freezing temperature of the rest of the droplet population.

The authors use the Broadley et al. data as an “absolute data set” meaning the uncertainty of the data and its implication for the application of this model is not considered. In this study it is emphasized that the nucleation process is stochastic in nature whereas Broadley et al. do not assume this. The Broadley et al. data likely possesses a large statistical uncertainty when stochastic processes are implied. Furthermore, the ice nucleating surface area in each droplet will be uncertain. As stated in figure caption 5, droplets with diameters 10-20 μm were applied. This results in about one order of magnitude uncertainty in surface area. This uncertainty alone would consolidate all curves shown in Fig. 5. In other word, this uncertainty nullifies attempted analysis and proof of the validity of the assumption of internal and external variability and suitability of this parameterization. Again, the presented approach may have some validity but it is very poorly executed by just looking at one data set and not discussing the uncertainties of the data set. Furthermore, the authors mention that they performed cold stage freezing experiments but these data are not shown. Why not making a stronger case, if there is the data?

In summary, the manuscript should clearly communicate the assumptions and caveats of the model and the data investigated. No molecular processes are directly observed or measured. Any interpretation in this regard should be suggestive, speculative, hypothetical in wording reflecting the nature of this mathematical exercise. There is no loss by doing this. Time will tell if this was the correct way for yet unknown reasons. The manuscript about a new model would be much stronger when tested using different experimental data.

p.1, l. 13-19: The 2nd sentence of the abstract lacks carefulness. Other researchers would claim their parameterizations are consistent with their experimental studies since they describe frozen fraction curves for changes in area, time, etc. There is no clear definition for “consistent” or “comprehensive”, and “freezing properties”? The following sentence then introduces the model with the statement that it uses a continuous function of contact angle and no restrictions on actives sites. These statements are somehow misleading. Fact is, the model can reproduce experimental data.

p.1, l. 26-27: The authors write “the two-dimensional nature of the ice nucleation ability of aerosol particles”. What is the meaning of this? The only way I can make sense of

this, is assuming that external and internal particle mixtures are meant by this?

p. 2, l. 2-5: This sentence has to be reworded. A distribution cannot be statistically significant.

p.2, l. 6: “will not” This exemplifies a claim of certainty, when in fact this is based entirely on a model assumption of some active site surfaces. As mentioned above there is no direct experimental evidence for an internal/external active sites.

p. 3, l. 13-14: The results of Vali (2008) do not show there is a strong spatial preference because this could not be directly measured. Vali (2008) might have claimed his experimental results suggest there are active sites in preferential locations (based on mathematical analysis).

p. 3, l. 16-19: The role of time for what? This is very sloppy discussion and does not reflect the community’s concern on this issue besides lacking important laboratory work from Koop, Knopf, Lohmann, and others and field work indicating the important role of time to explain observations. This section has to significantly improve if time dependence is addressed in this manuscript. As it is, the reader is left pretty clueless and cannot do more than accept written statements.

p. 3, l. 20: “completely”? What is meant by this?

p. 3, l. 29 - p. 4, l. 2: This is in principle the repetition of previous sentence describing the findings by Ervens and Feingold. However, here it is somehow generalized: What models? What results? Why are their more drastic variations?

p. 4, l. 3: “First principles of classical nucleation theory”. This is a strong claim. I would much doubt that the authors show any derivation from first principles in this manuscript. There is no discussion or derivation of clustering, free energy changes or chemical potentials, capillary approximation, etc.

p. 4, l. 5-8: “accounts for the variable nature of an ice nucleant’s surface and the distribution of ice active surface site ability across a particle’s surface (internal variability), and between individual particles of the same type (external variability)." This must be much more careful formulated. There is no direct evidence for the variable ice nucleating nature of a particle surface or the surface of different particles. This is an assumption the authors make based on previous work that predisposed this assumption into a mathematical fit. Also, on l. 5, ice embryo growth and dissolution is part of classical nucleation theory. This is part of a testable physical theory, but not "proven" to occur. The authors need to recognize that even an ice embryo is theoretical. The existence of a g-distribution is even less so as it serves a mathematical scaling or integrating fitting function, not something physical.

p. 4, l. 10: "and interpret". This model cannot interpret the freezing data since it is not based on a testable theory. Its assumptions cannot be proven and a g-distribution cannot be measured. The authors want to interpret freezing as the result of active sites, when in fact they already assume that the presence of active sites result in freezing. This indicates circular reasoning. Although, it is sufficient to say that this approach can successfully describe the freezing data - a valuable result.

p. 5, l. 17-19: Reflects a misunderstanding of the authors about CNT. 1. "pure" makes no sense here. 2. CNT does not assume/indicate that ice nucleation occurs uniformly across a particles surface. This formulation considers only an embryo on a surface. 3. A particle surface area is not included in Eq. 2, this is because there is no dependence on particle surface area. Maybe the authors assume that the contact angle is uniform over the entire surface and from this, when applying Eq. 2 over the whole particle surface, infer that ice nucleation ability is uniform across the entire surface. In other words, CNT has never made any assumption of uniformity of particle surface areas, but a single contact angle is only conceptualized by previous studies in the literature. It is not a facet or constrain of CNT. This should also be changed on p. 8, l. 12-14.

p. 5, l. 22: Equation 3 can only be formulated assuming that every particle has the same surface area. The authors define A as the surface area of a single particle. Then this A must have an index for each particle? The assumptions for this equation are not

clear and are misleading.

p. 6, l. 3-6: "A more realistic approach is to recognize" is a very bold statement. How about "We assume…"?

p. 7, l. 1-8: Maybe make clear that these are the authors' definition of internal and external variability. This does not represent text book knowledge and agreed-upon-facts.

p. 7, l. 9-11: This is a misleading statement and should be discarded. There is no proof that this approach provides direct insight. The authors are assuming variability without showing that particle surfaces are considerably variable in terms of their ice nucleation ability. Again this is a mathematical construct.

p. 8, Eq. 8: J, per definition, is not a function of time but of temperature. Here, this is only the case because via the cooling rate it gives temperature. This is confusing when coming from CNT and not necessary. One could start with Eq. 9.

p. 8, l. 16-21: This is an example, where the authors show no sensitivity that their approach is mathematical only, but use the good fit to make firm statements about the underlying process for which there is no proof/direct observation. In fact, other fit-based studies could claim the same. For now, these are non-testable statements and should be avoided.

p. 8, l. 22 to p. 9, l. 6: This section has to be improved. This is too difficult to understand in terms of what has been done mathematically to derive the freezing probabilities. I am left with several assumptions how to proceed.

p. 9, l. 17-22: Again, strong statements for an effect that cannot be fundamentally proven as of yet and that can also be described by other mathematical/physical means. Why not frankly state something like: "These results suggest that …may…may… though previous parametrizations have also been able to describe…". I assume the authors want to put out this new idea, something to further investigate in the future...

p. 9, l. 27- p. 10, l. 1: This text section states that a g distribution is just a probability density function that indicates the numbers of sites with a certain θ. But the text starting on p. 15, l. 8 states that the authors draw θ from a uniform distribution and then calculate g(θ)? So g is not a probability that particles have a certain θ value? Does this mean every θ from 0 to 180° has an equal chance to be present on the surface of particles, but freezing probabilities are scaled by the integrating factor g(θ)?

p. 10, l. 4- 8: This is very confusing. First somehow one large active site is assumed (summing up surface area) but then it is stated that this active site (which by definition has one nucleation probability) has a continuum of ice nucleation activities.

p. 10, section 3.2: Why not plot the continuous distributions used in this work including the approximated one and full one (g and g_bar)? Could be added as a supplement.

p. 11, l. 12-21 and following: Again, very firm statements on the underlying molecular processes not treated by the mathematical formalism. Statement of active site size is incorrect. CNT does not give size of active site but gives size of a critical ice embryo for given supersaturation. That this somehow, potentially reflects the size of an active site is very speculative and questioned by most recent findings using molecular dynamics simulations (e.g. Cox et al., 2013, Zielke et al., 2015). The fact is that a number can be calculated by integrating Eq. 11, but this is only a result of your assumption of a g distribution. It does not give significant insight.

p. 12, l. 25 – p. 12, l. 2: These general statements are incorrect. See general comments above. There are other types of cold stage experiments that apply micrometer-sized droplets and INPs with surface areas that are atmospherically relevant. Also, this manuscript does not give a fundamental proof that studies using large particles result in erroneous nucleation descriptions. If so, this would have ramifications far beyond the area of atmospheric sciences.

p. 12, l. 7-9: This is confusing, also due to above issues of definition of variability. The frozen fraction curve resembles freezing of droplets not considering the INPs inside

it. The Murray group observes a subset of droplets freezing differently than others, suggesting external mixtures. A few lines above, one large particle in one large droplet is described and here one large droplet with many small particles is considered, but still within one droplet. In fact many small particles should express a larger surface area. The effect of many small cannot be resolved since only freezing of that one entire droplet is observed.

p. 12, l. 16-18: Poor wording: “threshold of statistical significance”. Of a distribution?

p. 12, Eq. 12: Until now the word ‘system’ has been something general, but here is there a specific definition to this? What is one system? What is the ith system? Is a single droplet a system, is a single particle a system with active sites, etc.? Be consistent throughout the document.

p. 13, l. 14-22: Reword to express more suggestive nature of results.

P. 13, l. 23: Poor wording: “threshold of statistical significance”.

p. 14, l. 1: What are high particle concentrations? Whose data are you using here? Should be stated in the beginning of this section. What is a retrieved averaged g distribution?

p. 14, l. 7-31: It seems discussion starts with the right panel of Fig. 4. Why not plotting this one in the left panel? Please add experimental data as well to show model representativeness.

p. 14, l. 22-24 and l. 27-30: Your approach is successful, but only due to the assumptions used in simulating the freezing. This does not mean that it actually happens in your sets or Broadley et al., 2012.

p. 15, l. 1-5: This is important. When introducing a new model, it has to be evaluated by different data sets. Why are these results not shown?

p. 15, l. 6-11: Isn’t a running index for g(theta_r) missing to indicate that the calculation is performed for each individual droplet? Somehow this is missing here and above in the manuscript. In other words g is subsampled to find the contact angle that causes freezing of that particular droplet within the given frozen fraction curve?

p. 15, l. 12-19: See general comments above. When subsampling from g distribution (please present) with an arbitrary number of draws it is not surprising to represent the data. If I draw often enough, I can win any lottery without understanding the nature of the lottery. Can you present how often you draw for different data sets? E.g. a rare active site may have a probability of 10ˆ-10. Then you have to draw 10ˆ10 times. . ..?

p. 15, l. 21 and following: Please see general comments on uncertainties of experimental data sets.

p. 17, l. 1: The wording should be much more careful. As is it adds to confusion. What is a curve's behavior? What does it mean to be qualitatively and/or quantitatively captured?

p. 17, l. 7-9: I thought it is continuous. Why now arbitrarily dividing it in 1 nm2 segments? And why this size?

p. 17, l. 10-30: Again, this is only because of your assumption and does not give any evidence that it actually happens. It is acceptable to state that this paragraph is just your hypothesis and it may or may not be the case.

p. 18, l. 4-6: No, it is the first study that assumes it.

p. 18, l. 20-23: This statement, I feel, is a little unfair. The mathematical description of Broadley et al. (2012) were never designed to fit a global distribution and then fit again for the number of draws for smaller surface areas. As stated above, I don't feel that the authors' procedures are superior, just different.

p. 18, l. 24 – p. 19, l. 13: This section is also too strong in tone. It feels that the authors are dismissing all previous studies as inferior. The only difference between these studies is that different assumptions were made to represent their data. It suffices

to say once that the size of active sites are not assumed. The fact that other studies do assume this, does not make their parameterizations any better, worse or less correct.

p. 19, l. 14: What is meant by multicomponent? Different active sites? In addition, who said that they failed to be become a standard? If the authors want this sentence to remain in the manuscript and any other like it, they should write "It is our opinion that multi-component. . .have failed. . ." Studies by e.g. Hiranuma, Murray and Wex and others do not state that the multicomponent stochastic formulations have failed to become a standard in the way the authors write it.

p. 19, l. 20: "only". This method is computationally more demanding than others. The authors admit this on l. 29-30. Why emphasize at this point?

p. 20, l. 8-10: The word "trivially" should be taken out. It cannot be done yet. One cannot know the distribution of any ice active sites independent of an ice nucleation experiment.

p. 20, l. 29 – p. 21, l. 2: The authors do not know what individual atmospheric particles will or will not contain. Under giving assumptions, this is what your analysis suggests.

p. 21, l. 28-30: Again, tone: The authors write like a "statistically significant size cutoff" is proven to exist for atmospherically relevant particles. This is far from the case.

p. 22, l. 5: This statement is too strong and likely just wrong. The majority of the community would disagree with this.

p. 22, l. 10-17: What is the intention of this paragraph? This is too strong in tone. It also discredits all previous work. As stated above, the applied analysis does not allow such firm statements.

p. 22, l. 18-20: Again this holds only under given assumptions.

p. 23, 5: "If our assumption are true, then this would have consequences. . ..".

p. 23, l. 20: The previous paragraphs are written in such a way (like a summary and conclusion), that it felt that the paper should finish here. The authors might consider to place some of the said in the conclusions section.

p. 23, section 3.6: please see general statement. It could be completely removed and also the discussion on time dependence in the intro.

p. 24, l. 9-14: One could compare the impact of time on median freezing temperature with the work by Koop, Knopf, Lohmann groups. I believe, they find similar values using different approaches.

p. 24, section 4: To obtain a correct frozen fractions for smaller surface area, one needs laboratory experiments probing different particles sizes (to obtain and verify e.g. red curve in Fig. 4b). Why then is a correction factor h necessary? This h avoids drawing contact angles? As I understand it, the authors perform a fit obtaining g bar at surface areas above the threshold, subsample from g bar to get freezing curves surface areas below the threshold, then correct g_bar using h to overlap the subsampled simulations. . ... This overall procedure is hard to follow. I hope the authors can simplify this explanation. Please write this more concisely.

p. 26, Conclusions: I feel this is not a conclusion but more a summary, rather repetitive. A comment above points to text that could go here to make it a conclusion. The tone should be more suggestive in nature. It will need more studies to support the interpretation and to understand what it means on a molecular level for our understanding of immersion freezing processes.

Technical comments:

p. 5, l. 9: Avoid terms such as “simply”.

p. 7, l. 11: Omit “realistic”.

p. 13, l. 18: Omit reliably.

References:

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