Carnegie Mellon University

Department of Chemistry
Department of Mechanical Engineering
Center for Atmospheric Particle Studies

Professor Ryan C. Sullivan
Carnegie Mellon University
Pittsburgh, Pennsylvania 15213
Tel.: 412-268-8462
rsullivan@cmu.edu

July 13, 2016

Dear Dr. Grothe,

We have carefully revised our manuscript to address the referees' comments and feel we have now satisfied the majority of these. We have revised the title to "Effect of particle surface area on ice active site densities retrieved from droplet freezing spectra" from the originally "Using critical area analysis to deconvolute internal and external particle variability in heterogeneous ice nucleation." The new title better reflects the greater focus in the revised manuscript on the effect that particle mass and surface area concentration have on the ice nucleation properties retrieved from droplet freezing techniques.

The major improvement to the manuscript is the addition of droplet freezing spectra and their analysis for three particle systems obtained using our in-house cold plate instrument. Michael Polen, who performed the experiments on Snomax and cellulose, was added as an author as a result. The systems studied are Snomax bacterial particles, cellulose particles, and illite NX mineral particles – the same system studied by Broadley et al. that was the focus of our original manuscript. These three systems display similar inconsistencies in the retrieved ice active site densities (n_m or n_s) as particle surface area is varied as observed in the Broadley et al. illite data, further supporting our hypothesis that normalizing to particle mass or surface area in the droplets does not also always produce the same n_m or n_s value for the same particle system.

By randomly sub-sampling from the global $\bar{g}$ distribution of contact angle we demonstrate that we can predict how the slope and temperature position of the freezing curves shift with changes in particle concentration for these three systems, as was demonstrated for the Broadley data in the original manuscript. Furthermore, the $\bar{g}$ retrieved from the Broadley et al. illite data successfully predicts the freezing spectra of the illite data obtained in our experiments, after applying just a particle surface area correction. This supports the validity of the droplet freezing data obtained from our cold plate system, and the success of the $\bar{g}$ framework in describing a particle system's intrinsic ice nucleation activity.

By analyzing these four datasets on three ice nucleating particle systems and applying our g framework we have identified two effects that we hypothesize cause the variation in the n_m or n_s spectra retrieved from droplet freezing experiments. The first is a critical area effect, where total particle surface area concentrations below that system's critical area threshold produce larger values of n_m/n_s as particle concentration is further decreased. This is observed in the illite datasets, and the cellulose data. Snomax exhibits a different trend that is due to the unique and very strong ice activity of this system, as discussed in the manuscript. We propose that above the critical threshold no new more efficient ice active sites are introduced to the droplets by increasing particle surface area, and the retrieved n_m/n_s value therefore remains the same as particle concentration is further increased above the threshold. The other effect is a physical one that manifests as high particle mass concentrations, likely caused by particle coagulation and/or sedimentation. This artifact was recently discussed in *ACP* by Emersic et al., 2015.

The crux of our argument in the revised manuscript is that the surface area or mass normalization assumption that underlies the n_s/n_m framework warrants closer inspection and evaluation. The ice nucleation community has essentially been operating under the assumption that the same n_s value will always be retrieved from any proper method, regardless of how large a difference in particle concentration or surface area exists between methods. Inconsistencies in the n_s values retrieved using different methods for the same system (such as illite NX and cellulose MCC) are widely known and discussed in the community. This is often thought to be caused by differences between the methods used, and their inherent method artifacts. Particle coagulation and settling at high particle concentrations is one proposed method artifact, which we also suspect explains our highest concentration illite data. We are suggesting that the observed difference in n_s between methods and research groups may be more fundamental in nature and caused by changes in the distribution of active sites contained in particles sampled in the individual droplets that compose the arrays used in cold plate methods. We have presented experimental data from three systems and two research groups that demonstrate this variability in n_s as particle concentration and surface area are changed, and used our g analysis framework to interpret and propose an explanation for these effects. While we can agree we have not conclusively proven that our interpretation of the causes of these changes in n_s is the correct or only answer, we do not believe that there is available evidence that disproves our hypotheses. Considering the ongoing issues in reliably determining the concentration of INP and their ice nucleation properties/activity, a healthy debate that considers many possible explanations is warranted. This proposal is the main intent of our central hypothesis and the supporting data and analysis presented. Our discussion of the n_s framework and its application has been correspondingly revised in the text, and data from our cold plate system for Snomax, illite, and cellulose has been added to the revised paper to support our hypotheses.

We strived to clarify key terms and aspects of our analysis framework and to standardize the use of key terms such as ice active sites to address the referees' comments. We have clarified our analysis methodology as requested by the referees, and appreciate their extensive comments on our manuscript; these have undoubtedly helped to significantly improve the quality and clarity of our findings. We have replied to each of the referees' comments point-by-point in the document that follows, and hope that the revisions and additions made to the manuscript meet with your approval.

Sincerely,

Ryan Sullivan

Dr. Ryan C. Sullivan
Assistant Professor of Chemistry & Mechanical Engineering

Response to Referee 1 – Gabor Vali

… The explanation (scheme or model) proposed in the paper, and applied to the case in question, has three major areas of shortcomings. First, several points in the scheme are poorly defined, are counterintuitive, and/or are inadequately explained. This reviewer was unable to form a clear view of the reasoning in many places; his doubts are detailed in the list of comments that follow.

We thank the referee for his extensive and thoughtful comments on our manuscript. They have certainly helped us improve the quality and clarity of our research reported here. We have replied to each point in turn below, and revised the manuscript to address the concerns and questions raised. In doing so we have strived for increased clarity in our use of key terms, following the referee's many suggestions below.

Second, the focus of the paper on just one set of experiments is very limiting, specially since doubts are expressed even in the source paper about possible artifacts causing the unexpected results.

We acknowledge the concerns regarding our focus on just one set of experiments on illite mineral particles. To address this we have added experimental data and analysis recently obtained from our droplet freezing cold plate system for three INP systems: Snomax bacterial particles, cellulose particles, and illite NX mineral dust particles (as used in the Broadley et al. study). These three systems span the droplet freezing temperature range that can be accessed using droplet freezing methods. As we discuss below and in the revised paper, analysis of these three INP systems further supports the conclusions we present regarding the role that particle surface area and mass concentration play in affecting the observed droplet freezing temperature spectra and derived n_s or n_m values.

Third, the proposed model is restricted to interpreting only one specific type of laboratory experiment. It would be beneficial for the authors to first look at a wider set of data to see if similar patterns can be identified. Also, they would be well advised to consider alternative interpretations of the data in more detail than is evident from the paper. The theory proposed in the paper is not intellectually so attractive, in the form presented, as to make it of interest without clear explanations of what is meant by various new terms introduced, without showing success in quantitative interpretations of a variety of different types of data and without demonstrating improvements over other ways of examining the data.

We agree that the true test of any new model or theory requires demonstrating that it can successfully interpret or predict results from a wide range of experiment types. We have shifted the focus of the manuscript to using our framework to interpret and understand the effect of changes in particle concentration on the freezing temperature spectra. We do not attempt to fully demonstrate the accuracy of our framework in an absolute sense, and feel this exercise may not in fact be necessary as our framework is essentially an application of existing CNT formulations of heterogeneous ice nucleation, as the referee points out. We focus on droplet freezing experiments using varying particle concentrations at the same cooling rate as our motivation is to understand the frequently reported discrepancies in nm and ns values reported by different research groups using different methods, with different particle concentrations used. We have not focused on different cooling rates to explore time-dependent stochastic freezing effects as numerous studies have convincingly demonstrated that deterministic effects dominate over stochastic effects in the majority of systems studied under atmospherically relevant conditions. The referee's compilation and analysis of decades of ice nucleation data is a particularly impressive and convincing argument that stochastic factor play a secondary role compared to deterministic factors (Vali, 2014).

The paper is well written, as far as style and language are concerned. However, it is excessively long and contains a number of unnecessary repetitions.

We appreciate the suggestions provided below regarding repetitive sections that can be truncated or omitted, and have incorporated many of these suggestions as we explain below.

Even though it appears that this paper was written before the publication of Vali et al. (2015; Atmos. Chem. Phys., 15, 10263–10270), for the sake of easier communication the comments below employ some of the terminology introduced there.

We share the importance of using consistent terminology and have attempted to adopt the suggested terminology in Vali et al. (2015), and in the Referee's suggestions below.

[1] *Page 297 of Broadley et al. (2012): "It may be possible these high weight % droplets were not stable; as the concentration of clay-in-water suspensions is increased, flocculation and settling out of material can occur; hence, results from concentrated clay-in-water suspensions should be treated with caution."*

We agree that as the concentration of material in the water increases, physical processes such as particle coagulation and settling can occur, which in turn would lead to overestimating the surface area of the particles. This is a potential explanation for why freezing curves in the Broadley et al. (2012) exhibited a plateauing in freezing temperature when concentrations in their 10-20 μm droplets exceeded 0.15 wt%. In our recently conducted illite experiments, the results of which are reported in our revised manuscript, we see a similar effect above 0.25 wt% for our approximately 500 μm droplets. We also see a broadening of the freezing curves above 0.25 wt% that we think may be attributable to the inconsistent concentrations between the different droplets that could lead to a larger variation of surface area of the particles suspended. This is discussed in the revised manuscript on page/line 21/26-30 and 22/1-16:
"Another important conclusion that can be drawn from this dataset is that high concentration data (0.25 wt%, 0.3 wt%, and 0.5 wt%) exhibited a similar plateauing in freezing temperatures despite additional amounts of illite. This is similar to the concentration range where Broadley et al. (2012) found a saturation effect when further increasing the concentration of illite (over 0.15 wt%). This supports the hypothesis that the high surface area regime for illite experiments is actually a particle mass concentration effect and not a total surface area effect. The fact that the concentration where this saturation effect is so similar while the droplet volumes and consequently the amount of illite present between the two systems is quite different points to a physical explanation such as particle settling or coagulation due to the very high occupancy of illite in the water volume. These physical processes could reduce the available particle surface area in the droplet for ice nucleation. Additionally, the high concentration freezing curves show a good degree of broadening in the temperature range over which freezing curves. These three curves share a similar 50% frozen fraction temperature (with the 0.5 wt% oddly exhibiting a slightly lower 50% frozen fraction temperature than the other two). One explanation that is consistent with the hypothesis of particle settling and coagulation is that it becomes less likely that the droplets contain similar amounts of suspended material when they are generated from

such a concentrated suspension (Emersic et al., 2015). This results in larger discrepancies in surface area between the droplets and therefore a broader temperature range over which the droplets freeze."

[2]Laboratory experiments with suspensions of different concentrations of INPs from the same source, cooled at a steady rate, are examined and modeled in this paper. As argued in Vali (2014), such experiments with dispersed samples (drops) are effective for characterizing the INP sources (clay, etc.) but represent only one of many types of experiments that are needed to understand ice nucleation. Only combinations of several different experimental approaches constitute critical tests of interpretations, theories, or models. identified. Also, they would be well advised to consider alternative interpretations of the data in more detail than is evident from the paper.

We think we have strengthened our emphasis in the revised manuscript on identifying a particle surface area effect that impacts cold plate freezing spectra and is potentially a source for some of the discrepancy in retrieved n_s values for the same type of particles using different measurement methods. We present a numerical model that can describe the data and the trend this data exhibits. To strengthen our hypothesis we have added data from our own cold plate system. Please also refer to our response to your comment above regarding our experiment type.

6/6 The wording "discrete ice active surface site" needs to be explained more fully. Are the sites surface features that are assumed to be unchanged with time, or are they formations that develop randomly on the surface due to chance? I have the impression that the authors mean the former. If so, it should be clearly stated.

The sites are assumed to be surface features that remain unchanged with time. The wording has been changed to simply "surface active site" consistent with the terminology in Vali et al. (2014).

6/12 It is incorrect to refer to sites as being infinitesimally small. For the sake of allowing an integration to be indicated instead of a summation, it is sufficient for dA to be a small fraction of the particle surface area.

We agree and we have removed the reference to the sites being infinitesimally small and only refer to them as much smaller than the total surface area to allow for the integration.

7/6 - 7/8 Why would there be "differences in the g distributions" among particles of the same type? If It is because of their size differences, than they can differ because of the chance allocation of sites drawn from the same g distribution. Apparently you mean something different. Can you cite some reasons for why to expect that?

The hypothesis presented in the paper is that a difference in *g* distributions is due to a surface area dependence. Above a critical surface area threshold, *g* distributions are similar and below the critical area threshold *g* distributions are different because of chance allocation of surface active sites contained on each particle drawn from the global *g* distribution. We have clarified earlier on in the paper what our hypothesis is and how the observations we present support it, on page/line 4/8-26:

"A new parameterization, based on classical nucleation theory, is formulated in this paper. The new framework is stochastic by nature to properly reflect the randomness of ice embryo growth and dissolution, and assumes that an ice nucleating particle can exhibit variability in active sites along its surface, what will be referred to as internal variability, and variability in active sites between other particles of the same species, what will be referred to as external variability. A new method is presented to analyze and interpret experimental data from the ubiquitous droplet freezing cold plate method using this framework, and parameterize these experimental results for use in cloud parcel models. New insights into the proper design of cold plate experiments and the analysis of their immersion freezing datasets to accurately describe the behavior of atmospheric ice nucleating particles are revealed. Based on experimental observations and the new framework we argue that active site schemes that assume uniform active site density such as the popular n_s parameterization – a deterministic framework that assigns an active site density as a function of temperature (Hoose et al., 2008; Vali, 1971) – are unable to consistently describe freezing curves over a wide surface area range. This shortcoming is argued to be one of the causes of the discrepancies in retrieved n_s values of the same ice nucleating species using different measurement methods and particle in droplet concentrations."

8/24 - 9/6 If the drop is kept at a constant temperature of 255.5 K, how is a distribution of freezing temperatures obtained, as shown in Fig. 1 with the dashed-line curve,? This plot extends over ~5 degrees in temperature? Please explain.

The dashed lines in Fig. 1 are predictions of the freezing probability computed after a set amount of time passed for the whole temperature space, using Eq. (7). So we are computing the probability at each temperature for a constant elapsed period of time, *t*. The explanation has been modified to clarify this on page/line 9/15-23:

"Two droplet freezing probability fits (dotted lines) are also plotted in Fig. 1 under different environmental conditions. Instead of prescribing a cooling rate the freezing probabilities are generated by running Eq. (7) for the entire temperature range with each fit for $\Delta t = 1$ hour. One fit uses the same g distribution used previously, while the additional single θ fit is approximated as a normal distribution with a near zero standard deviation, similar to a Delta Dirac function. The resultant freezing probabilities are then computed and plotted for every T. It can be seen that the g fit retains much stronger time dependence, with the freezing probability curve shifting about 5 K warmer and the single θ curve shifting just 1 K warmer for the 1 hour hold time."

9/5 - 9/10 This is a prediction, with no empirical support. Right?

That is right. The prediction made here is not supported by experimental data that simulates the process. However it is consistent with previous findings with empirical support. We have clarified the text accordingly, on page/line 9/24-27 and 10/1-15:

"This numerical exercise shows that wider g distributions yield stronger time dependence due to the partial offset of the strong temperature dependence that the nucleation rate in Eq. (2) exhibits. The result emphasizes that how the active sites are modeled has consequences on what physical parameters (e.g. time, temperature, cooling rate) can influence the freezing outcome and observed droplet freezing temperature spectrum (Broadley et al., 2012). In Fig. 1 a wider g distribution resulted in higher sensitivity to time, which resulted in a shift of the freezing curve to higher temperatures as the system was allowed to temporally evolve at a fixed temperature. This significant change in the freezing probability's sensitivity to temperature is the cause of the more gradual rise in the freezing probability for the system when applying a non-Delta Dirac g distribution. This is effectively enhancing the stochastic element in the particle's ice nucleation properties. The shallower response of freezing probability to decreasing temperature (deterministic freezing) creates a greater opportunity for time-dependent (stochastic freezing) to manifest, as a larger fraction of the droplets spend more time unfrozen. The enhancement of the stochastic element brings about a more important role for time as shown in Fig. 1. The finding of this exercise is consistent with previously published work on time dependent freezing such as those reported by Barahona (2012), Vali and Stransbury (1966), Vali, (1994b), and Wright and Petters (2013), amongst others."

9/7 - 9/14 Why not test the calculations against the observed shifts in freezing temperatures with changes in the rate of cooling? Results from such experiments are described in Section 3.2.2 of V14.

Many studies have already conducted experiments to test time and cooling rate dependence as described in Vali (2014) and been tested against multicomponent stochastic models. We did not aim for the focus of this paper to be on time dependence but on the surface area dependence developed in the later sections. So we did not expand the analysis presented on time dependence to be fully comprehensive. We have added references to studies that have conducted a similar analysis and highlighted that what we are presenting here is merely our new framework supporting previous findings. Please see referenced text in previous comment above.

9/24 The wording "ice active site activity" is not a fortunate description. Suggest changing to something else.

The wording was changed to "ice nucleation activity".

9/27 - 9/28 "distributions" here refer to the g(θ) function?

Yes. We have clarified this in the text on page/line 10/19-20:
"There are, mathematically speaking, infinite solutions for the *g* distributions that produce a representative freezing curve."

9/27 - 9/29 To which side of the Gaussian curve does this comment apply? Please rephrase this sentence.

The comment applies to the ascending part of the Gaussian curve as the contact angle increases. The sentence has been rephrased to clarify this, on page/line 10/14-17:
"In any considered distribution an ascending tail with increasing contact angle represents a competition between more active but less frequent surface sites, and less active but more frequent sites."

10/4 - 10/8 Representing the distribution of sites of different potential activity as one site with a continuum of activity is very puzzling. I see no reason for doing this. Neither does it follow from the arguments presented about exponential dependence of freezing probability on J and exponential dependence of J on temperature. Please elaborate both on why this is useful to understanding the model and why it is justified.

We have omitted this representation of the distribution of ice active sites as one site with a

continuum of activity and replaced it with a representative spectrum of the particle's ice nucleation activity. This has been changed in the text on page/line 10/26-30:
"It is therefore sufficient to conceptualize that the particle has a well-defined monotonic spectrum of active sites increasing in frequency while decreasing in strength. The spectrum is modeled as a continuum of ice nucleation activity described by the g distribution, as depicted on the upper right hand corner in Fig. 2."

Fig. 2 The upper right inset and the second line of the caption are misleading and need to be corrected. The caption mentions " ... a representative effective ice active surface site " and the inset appears to indicate that the value of θ changes in concentric circles around a specific site. The histogram in the main part of Fig. 2 is a better representation of the information to be conveyed.

As mentioned in the previous comment, the reference to representing the distribution of active sites as one site with a continuum of activity has been removed and replaced it with a representative spectrum of the particle's ice nucleation activity. The inset in Fig. 2 is merely a visual representation of how active site strength anti-correlates with active site abundance (surface area) and is trying to convey the same message that the histogram of Fig. 2 is.

11/6 In Eq. 10 the right-most expression is approximately equal to the preceding expression with substantial differences for narrow range of integral limits. Thus, Eq. 10 cannot be "satisfied" – this sentence should be omitted.

The sentence has been omitted.

11/6 What case is being depicted here? The red curve is not the same as that in Fig. 1. What J-function is assumed?

The case being depicted here is that of an arbitrary g distribution. In the interest of consistency and clarity we have changed it to the case presented in the previous section and in Figure 1.

Fig. 3 Please indicate that θc1= 0 is assumed for this diagram. Also the value of μ and σ that were used.

It is now indicated that $\theta_{c1}= 0$ is assumed and the values of μ and σ are stated in the figure caption.

11/15 - 11/21 Is this example for case described in Section 3.1?

Yes. We have stayed consistent in the revised manuscript with what case example is being depicted to produce Figures 1, 2, and 3 to avoid confusion in that regard. This has been clarified in the text, on page/line 12/5-7:
"For the large ash particle system analyzed in the previous section (Fig. 1) it is estimated that for its estimated diameter of 300 μm and a cooling rate of 10 K/min $\theta_{c1} \approx 0.4$ rad and $\theta_{c2} \approx 0.79$ rad."

11/17 The estimate of site area is dependent on temperature and contact angle. The numerical value quoted should be referenced to the assumed values.

The estimate of the critical area is indeed dependent on temperature and total surface area. This has been clarified in the text. Please see previous comment.

12/10 Reference (2012) is incomplete.

Fixed.

12/10 --> The discussion appears to proceed as if particle count per unit volume of water was a single number. In fact different size particles exist in most cases, even when attempts are made to produce nearly monodisperse powders for laboratory tests. Thus, for the authors' argument to make sense, the monodisperse assumption has to be stated, or saturation of external variability need to be achieved for all sizes (probably impossible in reality). Also, it is implied that all particles have identical chemical and mean surface properties. Thus, the treatment here given applies only to laboratory experiments in which particles of a given substance are added to the water. These assumptions should be spelled out.

The treatment here applies to laboratory experiments in which particles of a given substance are added to water, this has been clarified in the text, please see posted text for the following comment.

The parameter of interest is not particle count per unit volume but total particle surface area per unit volume. Therefore, the monodisperse size assumption is not necessary. It is likely that a distribution of particles sizes exists within each droplet but the total mass of particles on average is similar between similarly sized droplets when taken from a well-mixed suspension. The surface area per droplet is then estimated from average mass per droplet using the experimentally determined surface area density as discussed in Broadley et al. (2012) and Hiranuma et al. (2014) among others. We have clarified this in the text, on page/line 13/5-10:

"For the application of this model to cold plate data where droplets are prepared from a suspension of the species being investigated, the particle population in each droplet is treated as one aggregate surface and a mean surface area value is assumed for particle material in all the droplets in the array. This estimate is retrieved from the weight percentage of the material in the water suspension and our best guess for a reliable surface area density."

12/25 What does 'one system' mean?

In the original manuscript we referred to a particle as a system and as well as a species under study (i.e. illite). We have corrected this in the revised manuscript and one system refers to a particle species under study. In this case system was referring to particle but this description has been removed, on page/line 13/16-17:

"and $P_{uf,i}$ is the probability that the particle *i* does not freeze. Further expanding the expression yields:…"

12/27 What is system i ? One particle?

Yes. This was clarified in the text as described above.

13/16 This critical area notion is in contradiction with the monotonic decrease of g(θ) as θ approaches 0, i.e. in principle this critical area can only be reached with nucleation at the melting point (e.g. 273 K). If the lower limit θc1 ≠ 0, the definition may make sense but remains of questionable practical meaning.

Since the *g* distribution is defined by a Gaussian function with a standard deviation there is a limit to how small the surface area can be for it its active sites to be defined with a continuous function as such. Strictly speaking for every surface area there is a limit to which active sites exist as the contact angles on the tail of the *g* distribution depend on a certain amount of surface to exist for their probability of being on the particle to become greater than zero. Thus for any surface area there is a contact angle range in which the probability of active sites possessing these contact angles is neither 100% nor 0%. This in principle is a contact angle range that requires a discrete statistical treatment. We think that for large particle surfaces differences between particles in ice nucleating ability is less substantial than particles with small surfaces because this contact angle range starts to have more impact for smaller surfaces. The analytical treatment of this is a topic of ongoing research we are engaged with, the details of which will be presented in a forthcoming manuscript. Here we focus on the effect that particle concentration has on the observed freezing temperature spectra and the n_m or n_s values derived from these.

13/25 - 14/6 Again, experiments are mentioned without stating that a specific type of experiment is being discussed. This has not been clearly established in the foregoing. This is a serious constraint on the applicability of the scheme developed in the paper and need to be fully explained at least at the beginning of Section 3.3, specially since a different type of experiment in discussed in Section 3.1.

We have added more emphasis on how the scheme developed is mainly done for a specific kind of experiment, using a fixed cooling rate. Throughout the paper and especially towards the end we highlight further the advantages of cold plate experiments to investigate the hypothesis presented. Since we are studying a surface area effect, the cold plate is a practical tool to span the surface area range of particles of interest. We have revised the text accordingly, such that the beginning of section 3.3 states the type of experiment the model is applied to on page/line 13/5-10:
"For the application of this model to cold plate data where droplets are prepared from a suspension of the species being investigated, the particle population in each droplet is treated as one aggregate surface and a mean surface area value is assumed for particle material in all the droplets in the array. This estimate is retrieved from the weight percentage of the material in the water suspension and our best guess for a reliable surface area density."

14/4 Can the authors spell out what they consider significant divergence?

We have changed the wording from significant divergence to a more elaborate explanation of how the prediction in this case neither captures the onset of freezing of the frozen fraction being studied nor the range of temperatures the curve spans (i.e. the temperature space over which freezing is happening). On page/line 14/21-24:

"The particle number or surface area concentration is then decreased until the retrieved g distribution (from the measured droplet freezing temperature spectrum for an array of droplets containing particles) can no longer be reasonably predicted by $\bar{g}$."

On page/line 15/10-17 is an example of further elaborating on when the frozen fraction curve is not captured by $\bar{g}$:
"Moving to the lower concentration freezing curves (1.04×10^{-6} cm^2 – 5a; and 7.11×10^{-7} cm^2 – 4a) the transition to below the critical area begins to be observed. The solid lines attempt to predict the experimental data points using $\bar{g}$. Predicting experimental data points for the 1.04×10^{-6} cm^2 (5a) system with the same $\bar{g}$ distribution captures the 50% frozen fraction point but fails at accounting for the broadness on the two ends of the temperature measurements. The prediction from $\bar{g}$ completely deteriorates in quality for the lowest concentration experiments (7.11×10^{-7} cm^2 – 4a) as it neither captures the temperature range over which freezing is occurring nor the 50% frozen fraction point."

14/15 - 14/16 This sentence is crucial to the view represented in the paper: " ... variability of active sites remains constrained within droplets." The authors view is focused on the distribution of contact angles (as a proxy for real factors). This is expressed by talking about variability remaining constrained in the drops, i.e. an attempt to separate what they call external and internal variability. Diluting any sample containing suspended INPs and thereby the reducing the particle content per drop volume used in an experiment has been found to lead to lowering of freezing temperatures in numerous experiments. This results in retrieving a different segment of the ns(T) or k(T) spectra (Fig. 4 in Vali 1971 and many later examples). The data plotted as the fraction frozen versus temperature may or may not show a change in shape, depending on whether the slope of the ns(T) or k(T) spectra happens to change over the observed range of freezing temperatures.

The $n_s(T)$ spectra retrieved experimentally for the systems presented in the paper (we have added our own experiments using illite NX, Snomax, and cellulose containing droplets) all show large variations as the concentration of material in the droplets is lowered. The difference in n_s cited here isn't just in the shape of the curve but in the values of the parameter at the same temperature. We have used small changes in concentration to achieve good overlap of the different $n_s(T)$ curves in temperature space. This demonstrates that n_s at the same temperature does indeed change as particle mass concentration in the suspension used to prepare the droplets is changed. This has been clarified in the text in two paragraphs, on page/line 19/24-30 and 20/1-27
"The values of n_s were retrieved directly from freezing curves of droplets with illite particles immersed in them measured in a cold plate system by Broadley et al. (2012) and used to produce the right panel in Fig. 4. As the total particle surface area of the system under study is reduced from the blue to the red curve, the retrieved n_s values are similar indicating that variability of active sites remains constrained within droplets. Note that both the red and blue curves were obtained from systems we have determined were above the critical area threshold (Fig. 4). Further reduction of total surface area to below the critical area threshold shifts the n_s values noticeably, as seen by the significant increase in n_s(T) for the green curve. As all three curves were obtained by just varying the particle concentration of the same species the same n_s values should be retrieved for all three curves; the n_s scheme is designed to normalize for the total surface area or particle mass present. This is successful for the higher particle surface area systems (red and blue curves are similar) but not at lower particle area (green curve diverges). The large increase in n_s observed when total surface area is below the critical area threshold indicates that the observed droplet freezing temperature spectra do not just linearly scale with particle concentration or

surface area. Further analysis will show this is not due to an enhancement of ice nucleating activity per surface area but is actually a product of external variability causing a broadening of the ice nucleating spectrum within the droplet ensemble when total surface area is below the critical area threshold.

We have observed other similarly large effects of particle concentration on the measured droplet freezing temperature spectrum and the retrieved n_s curves from our own cold plate measurements. The right panels in Figs. 6 and 7 display n_s curves versus temperature for freezing droplets containing Snomax or MCC cellulose, respectively. Similar to the data in Fig. 4, these two systems also exhibit a divergance in n_s as concentration (or surface area) is decreased. Droplets containing MCC cellulose exhibited a much stronger sensitivity to decreasing surface area than the droplets containing illite did, with changes in the values of n_s of up to four orders of magnitude. The droplets containing Snomax on the other hand were less sensitive to changes in surface area and exhibited an opposite trend in n_m (active site density per unit mass(Wex et al., 2015)), with the values of n_m *decreasing* with decreasing concnentration. This is consistent with the analysis of the Snomax freezing curves, where the ice nucleating activity experienced a substantial drop with decreasing surface area. It is further argued in a later section that this is due to the very sharp active site density function *g* that Snomax particles appaear to possess, resulting in steep droplet freezing temperature curves."

Fig. 4 in Vali (1971) shows the cumulative nucleus spectra for three samples of different surface area. Their overlap (within error) within the framework presented in our manuscript is due to the high surface areas of material the drops of large volume contain. Melted hailstones contain a much larger particle surface area (and consequently active sites) than cloud droplets by virtue of them being the added sum of many cloud droplets and rain drops. Therefore, it could be argued that these samples contain enough material to exhibit similar active site spectra per drop for the range of drops considered. On the other hand, the n_s plot newly introduced into the paper in Fig. 7b demonstrates that n_s values retrieved from the frozen fraction curves from different particle mass/surface area concentrations can span several orders of magnitude in n_s at the same temperature.

14/24 ".. green curve diverges ..." is an incorrect interpretation of the experiments discussed. It is not plausible for a well controlled experiment with a stable suspension of INPs to produce higher freezing temperatures (higher fraction frozen of higher ns values) with a reduced particle content per drop.

It has been clarified that for the same suspension of INPs it is not plausible for higher freezing temperatures to occur upon reduction of the amount of material present in the sample. However, we do see quite similar freezing onsets even after the reduction. This contributes to the inflated n_s values since n_s is a cumulative function and the freezing temperature of the first droplet in the array affects the n_s values retrieved from all the subsequently freezing drops. Our explanation is that the active site spectrum that had been approximately contained at high surface areas, is at the lower surface areas distributed between different droplets. So the reduction in surface area of particles in the droplets resulted in more variability between the active site spectra between the different particle containing droplets. Active site distributions (n_s or $\bar{g}$) that were able to describe the frozen fraction curves for the higher surface area experiments, are unable to capture the early onset of freezing or the broader temperature range over which freezing occurs because they do not account for this change of active site spectra within the reduced surface area particles. The underlying hypothesis is that some particles now contain stronger active site spectra than their higher surface area counterparts, while some contain weaker active site spectra. If hypothetically these small particle surfaces were combined and produced a surface area higher than the critical area, their resultant active site distribution would be that which can be modeled using n_s or $\bar{g}$.

15/1 - 15/5 These data should be presented.

New cold plate data for illite, cellulose, and Snomax have been added to the revised version of the manuscript.

15/8 - 15/15 This description is difficult to understand. How does the particle surface area influence the result from Eq. (16)? The total surface area of the particles within each drop is the parameter that is modeled, yet it does not appear in the description. What do you mean by optimizing the choice of ndraw?

What is being modeled is actually the *g* distribution of the particle material within the droplet. Surface area influences the result directly in the application of Equation (16) and indirectly in that n_{draws} scales with surface area roughly. As the surface area of the system being modeled was decreased, n_{draws} also decreased. More details about the method have been added to show that n_{draws} is a very soft optimization parameter; the value of n_{draws} used for the systems presented here ranged from 65 to 9 draws. We choose the n_{draws} value that creates an array of *g* distributions (one for each droplet) that achieves the best prediction of the experimental data. It is thus the single optimization factor used to produce the predicted freezing curves, sub-sampled from the global $\bar{g}$ distribution obtained from the high concentration data. This is described in the new text, on page/line 17/1-22:

"To predict the freezing curves of the droplets with particle surface areas lower than the estimated critical area for the systems considered here, the aggregate surface area of the entire particle population within each droplet is modeled as one large surface. A contact angle θ_r is randomly selected from the full contact angle range [0, π], and the value of active site distribution g^* for the particle *i* being sampled for at θ_r is assigned the value of $\overline{g(\theta_r)}$:

$$\left(g_i^*(\theta_{r,n_{draw}})\right) = \overline{g(\theta_r)} \qquad (16)$$

The g distributions within this numerical model are given an asterix to indicate that they are discrete distributions.

This process is repeated for a parameter n_{draws}, for each droplet in the array that produced the freezing curve being modeled. n_{draws} is the only parameter that is optimized for so the modeled freezing curves can predict the behavior of the experimental freezing curves. The value of n_{draws} typically ranges from 9 to 65 for the systems analyzed here and is therefore a relatively soft optimization parameter with small dynamic range. The sampled g^* distributions are normalized with respect to the estimated total surface area for the freezing curve being modeled before being used to compute the freezing probability. The bottom part of Fig. 4 shows a schematic of how g^* is retrieved from $\bar{g}$ using n_{draws}. With the sampled g^* distributions the freezing probability of each droplet is calculated using Eq. (9) and the frozen fraction curve is computed from the arithmetic average of the freezing probabilities:

$$F(below\ critical\ area) = \frac{1}{N}\sum_{i=1}^{N} P_{f_i} \qquad (17)$$

where N is the number of droplets in the cold plate array."

16/7 - 16/8 This statement cannot be supported because of the limited scope of the evaluations made in this paper. It may refer to some apparent problems in the Broadley et al. (2012) paper to see how the data can be reconciled with the description based on surface site density. Shifts in the F(T) curves with no change in shape is not a requirement at all for the applicability of the interpretation of observations in terms of ns(T) or k(T) spectra. The note above for 14/15 - 14/16 explains this.

We have clarified in our revised version of the paper that it is not the shifts with no change in shape that create the arguments for non-uniform active site density below a critical area, but the different values of $n_s(T)$ retrieved directly from the observations. We think that a single active site density function assumption breaks down by virtue of reduction in surface area. If a particle is partitioned enough times, there is a breakdown point after which some particles will carry a denser distribution of activity than others (we discussed this in an earlier comment above). The broadening of the curves combined with the early onset of freezing that just cannot be predicted by a single active site density supports the hypothesis presented.

16/12 - 16/14 Is the g-bar distribution determined using Eq. (9)? If so, is the integral over contact angle applied as indicated (0 to π) or some smaller range? It would appear illogical, as it is also argued on page 10, to consider both the ascending and descending parts of the normal distribution. The details of this fit should be clearly described in the text for the process to be comprehensible to readers. The fit being determined for experiment (6a) is used for (6b) which has approximately factor 3.7 higher particle surface area. Thus, the frequency values extracted from g(θ) are reduced by about the same factor. While this is a fairly small factor compared to overall range of values needed to reproduce the freezing frequencies, it is important to know what part of the Gaussian curve comes into play.

Yes, $\bar{g}$ is determined using Eq. (9). We do consider the full contact angle range when carrying out this fit, even the descending part. While the descending part doesn't contribute to the freezing behavior it is part of the Gaussian function, which we have decided to use out of convenience. The Gaussian distribution is determined by two parameters that are relatable to the process being modeled, with the mode determining how strong/active the g function is and the standard deviation determining how much variability among active sites there is. A cumulative density function does the same job and does not have a descending tail, but we have worked with a Gaussian function throughout the process of building the framework and there is no computational advantage to using a cumulative density function over a Gaussian. So while the descending part of the curve is redundant, it does not take away from the convenience of using this kind of distribution.

When the same $\bar{g}$ is determined to predict experiment (6a) the entire contact angle range is thus considered. The details of the fitting procedure have been clarified in the text, on page/line 15/8-10:

"The fit to the 6b curve is done using Eq. (9) and follows the same procedure of least square error fitting described in section 3.1."

16/29 - 16/30 Following the questions raised in the preceding two comments, is the random draw taken from the entire g-bar function, i.e. for 0 < θ < π?

The random draw is carried out over the entire contact angle range. We have clarified this detail on page/line 17/3-6:
"A contact angle θ_r is randomly selected from the full contact angle range [0, π], and the value of active site distribution g^* for the particle i being sampled for at θ_r is assigned the value of $\overline{g(\theta_r)}$."

17/10 - 17/26 Understanding of this paragraph is hindered by the use of expressions like "very active" when the model is constructed around the idea of a continuum of activities, albeit of different frequencies of occurrence. Similarly, 'leftover" drops goes counter to the model. There is no surprise in the fact that lower concentration of INPs lead to lower freezing temperatures. That there are a small numbers of freezing events at similar temperatures than for the higher surface area drops is due only to the relatively small change in the total surface area per drop. For any given temperature at the warm tail of the distribution the frequencies of these events can be expected to scale with surface area of INP per drop.

The text has been modified to clarify we are discussing the range of activity over single active sites, as that is more consistent with how the framework is constructed. The droplets freezing at lower temperatures lack the ice nucleating potential of the droplets freezing earlier because of lower active site density. In an absolute sense there are a smaller number of freezing events with the reduction in total surface area per drop. It is how this reduction of freezing events is occurring that is of particular interest. The droplet freezing behavior is changing inconsistently, that is some droplets retain a very warm freezing temperature (close to the temperature of droplets with higher surfaces areas) and some droplets are freezing at temperatures lower than expected with the reduction of surface area. It appears that for two of the systems studied here, cellulose and illite, at the warm tail of the distribution the frequencies of freezing did not scale with surface area per drop. The text has been revised on page/line 18/11-28:
"Perhaps the most notable characteristic is how these freezing curves ascend together early as temperature is decreased but then diverge as the temperature decreases further. The closeness of the data at warmer temperatures (the ascent) is interpreted by the framework as the presence of some rare high activity active sites within the particle population under all the particle concentrations explored in these experiments. At lower temperatures it appears that there is a wider diversity in the activity of droplets that did not contain these rare efficient active sites, and thus there is significant spread in the freezing curve for $T < 242$ K. In the context of the framework presented here this can be attributable to strong external variability of the ice nucleating population, with very strong/active nucleators causing similar freezing onsets for different particle concentrations at the warmer temperatures, and a lack of strong nucleators explaining the less consistent freezing of the unfrozen droplets at lower temperature. Thus it follows that there is a wider spread in the freezing curves for these droplets, as their freezing temperature is highly sensitive to the presence of moderately strong active sites. This expresses a greater diversity in external variability – the active site density possessed by individual particles from the same particle source. In a later section the claim of more external variability contributing to the broader curves below the critical area threshold is supported with a closer look at the numerical results from the model."

19/6 - 19/8 The criticism of pervious works for not having distinguished above and below "critical threshold" conditions sounds hollow, since the idea of critical threshold is introduced only in this paper. The real test is whether those previous treatments were successful, or not, in representing all aspects of the empirical data.

This has been removed as a criticism in the text. We were simply pointing out that this is the first work to identify this surface area dependence. It does provide some success in explaining discrepancies in active site density retrievals using different methods, shown in the new plot in Fig. 11 for example.

19/14 --> Again, contrast is drawn with previous work in a way that only focuses on differences in procedure not on the success of the interpretation. In any case, no theory can be considered of general validity when it applies only to laboratory preparations with a series of suspensions from the same source of INPs and in one specific manner of testing.

Emphasis has been added on where the framework presented here is successful in its interpretation that others are not. We do not consider this a theory that is generally valid, but rather an attempt at explaining the surface area dependence identified here that previous work has not explored. That is why thus far the framework has dealt with this specific manner of experimental testing, as it is the best way to isolate the parameter of interest. We have added two other sources of INPs to further support our hypothesis, however, as well as our own measurements of illite particles.

20/17 - 20/18 This has been a limitation of this paper from the beginning. The fraction frozen curves are incomplete representation of the information content of the data.

Yes, we agree that they are an incomplete representation. However, we argue that they provide evidence of the presented hypothesis when spanning a range of mass/surface area concentration. Active site density retrievals from these curves that don't overlap in the same temperature range is, we think, evidence that there are surface area dependent changes that can't be accounted for using surface area normalized active site density functions. This is discussed in the text on page/line 27/13-30 and 28/1-2:
"The critical area analysis carried out in this paper emphasizes the dangers in extrapolating the freezing behavior of droplets containing a large concentration of particle to droplets containing smaller concentrations. Applying a parameterization such as n_s directly to systems below the critical area threshold in a cloud parcel model for example yields large differences in the predictions of the freezing outcome of the droplet population. As the concentration of the species within the droplets was decreased in the cold plate freezing spectra considered here the actual freezing temperature curves diverged more and more from those predicted when the systems were assumed to be above the critical area. This led to significant changes in the retrieved n_s values, as shown in Figs. 4, 6b, and 7b. The large effects of concentration on the droplet freezing temperature can be directly observed in the frozen fraction curves plotted in Figs. 5, 6a, and 7a. Differences between observed frozen fraction curves and ones that assumed uniform active site density yielded errors in the temperature range the droplets froze over as well as the temperature at which 50% frozen fraction point. Therefore, a cloud parcel model would be unable to accurately predict the freezing onset or the temperature range over which freezing occurs using a single n_s curve obtained from high concentration data. This has important consequences for the accurate simulation of the microphysical evolution of the cloud system under study such as the initiation of the Wegener–Bergeron–Findeisen and the consequent glaciation and precipitation rates (Ervens and Feingold, 2012; Ervens et al., 2011)."

21/2 What is meant by 'freezing behavior'? If it refers to the breadth of the F(T) curves, that represents a narrow view of what the empirical data indicates.

Freezing behavior of the droplets is meant to refer to how the freezing curves have changed with surface area. Of particular interest in this work was how with surface area reduction the frozen fraction curves of the systems considered retained a similar onset of freezing and froze over a broader temperature range.

20/2 - 23/10 Most of the four pages of Section 3.5 is an unnecessary repeat of the features of the proposed model.

We have reworded some of this section to avoid unnecessary repetitions. The critical area analysis carried out is unique to this section however and we think provides a closer look at why the freezing behavior changes the way it does with decreasing surface area. We have also added a new plot in Fig. 11 that highlights how much of the discrepancy in active site density retrievals with different measurement methods is actually spanned by the surface area dependence presented here as well as the suggested concentration saturation effect. We now hope that this section is less repetitious and has more standalone value.

Response to second set of comments from Gabor Vali:

Since much of the material presented in the paper depends on it, the meaning of the critical contact angles and of the critical area needs close scrutiny. These terms are defined on pages 11 and 13 of the paper.
The notion underlying these definitions is that the range of activity for any given substance has upper and lower limits other than the melting point and the homogeneous nucleation threshold. These limits are expressed as the smallest and largest contact angles possible (θc1 and θc2) on the given material. Contact angle is used as a convenient parameter to quantify activity in terms of CNT. The lower end of the range of activities, established by θc2 is less interesting as it corresponds to a high number of possible occurrences, while values near θc1 correspond to rare cases of high activity (freezing temperatures). If this interpretation is correct, the critical area can be stated with Eq. 11, replacing in it g by g-bar. The method followed in the paper for determining g-bar and the critical contact angles θc1 and θc2 appears to consist of fitting Eq. 15 to he F(T) curve for the highest particle loading in Fig. 5. This is unclear in the paper as the integration limits in Eq. 15 are given as 0 to π. It would be useful to have the authors' clarification on this.

The introduced concepts of “nucleating area”, defined in Eq. (11), and the critical area, the smallest area satisfying Eq. (15), are not meant to express the same property. The nucleating area is an estimate of how much of the given surface of an ice nucleating particle contains the active sites contributing to freezing. The nucleating area depends on the total surface area of the given particle, the cooling rate (or temperature and time), and the g distribution. The critical area on the other hand is a hypothesized property of a given species. The framework presented states that given enough material a species can be prescribed an active site distribution $\bar{g}$ (n_s works equally well as a deterministic analog) and the total number of active sites scales with area in accordance with how equations (15) and (18) are formulated. In this high surface area regime, the active site frequency still varies with temperature however one function can describe the relationship so there is one value of n_s for each T. At surface areas below the critical area, it is hypothesized that chance allocation of active sites from a general distribution creates a discrepancy in the active site frequency between particles of the same surface area such that the value of active sites per unit surface is not the same for the particles. This is our explanation for why n_s values for the same temperature but retrieved from particles with different surfaces don't overlap below a certain surface area. While the critical area is a potentially inherent property of a species the critical contact angles are not. The critical contact angles depend on the specific freezing conditions and do not represent an absolute cutoff in the contact angles a particle can possess. That is why in retrieving $\bar{g}$ in section 3.3 and the subsequent sampling model we do not restrict the critical contact angle range. This was discussed in our response to the comment above regarding *16/29 - 16/30*.

We do however use the critical contact angle range to analyze in section 3.5 how the distribution of active sites characterized by the critical contact angle range differed between particles of different surface areas and of different species. We added a nucleating area analysis to droplets containing Snomax in the revised manuscript.

The plausibility of the concept of limiting values for θc1 and θc2 can be examined by looking at evidence in terms of spectra of INP concentrations either in terms of ns(T) or K(Tc)1. As far as I am aware of, no cases have been reported in the literature with sharp cutoffs in these quantities at either high or low activity values. The corresponding spectra may have steep slopes, but all have monotonic rise (with finite slopes) from the lowest temperatures detectable in given experiments to the maximum concentration values measured. The shape of the F(T) curve, or the temperature range it covers is related closely to a segment of the ns(T) or K(Tc) spectra and a shift of the F(T) curve along the temperature axis due to a change in sample volume is indication of the slope of the spectrum remaining constant the temperature interval covered. From the wide variety of spectra reported in the literature, it appears that assuming the existence of limiting values in activity is not justified. Of course, empirical data are subject to sample size and instrumentation limitations. Nonetheless, that is not the explanation given by the authors, so they should explain what a priori reasons they see for upper and lower limits of the contact angle, or of other measures of activity. Specific questions about how the assumption of critical area is supported in the paper, and about how it is used to interpret experiments, are raised in my first set of comments.

We hope that in our revised manuscript and in our responses we have clarified that we do not present the critical contact angles as properties of the system. Above the critical area the frequency of active sites will increase in accordance with equations (15) and (18) as temperature and surface area increase. So are there are no cutoff values for the quantities of $n_s(T)$ *or* $K(T)$ dictated by inherent cutoffs in activity. There are discrepancies in n_s values however reported in the literature and we present an argument that some of this discrepancy is attributable to the difference in sizes and thus surface areas of the particles investigated.

In case objections are raised about using ns(T) or K(Tc) for making the point in the preceding paragraph, it is important to recognize that over the relatively narrow temperature interval involved in the experiments being analyzed, the nucleation rate function J(θ) does not vary much in shape. Hence the dominant variations in the integral comes from g(θ) and that quantity is a measure of the frequency of different sites just as ns(T) or K(Tc) are. Also, such time-independent descriptions are adequate for examining questions like the existence of cutoff values in nucleating ability.

We agree with this.

From a practical perspective, there is likely to be a limit to how much material can be suspended in water for nucleation studies, so there is going to be a limit in the highest nucleation temperatures that can de detected in an experiment. However, going to a rather extreme example, it is a common observation that small puddles on soil have ice form on them when the temperature drops ever so little below 0°C. That the temperature didn't drop much below 0°C can be surmised from the fact that there is liquid water below the ice. While this situation is, clearly, a large jump from the laboratory experiments, and it surely involves many different types of INPs, the notion that no upper limit to heterogeneous nucleation exists other than the melting point is perhaps validly illustrated by it. The chance of encountering INP activity in any system decreases rapidly as the temperature approaches 0°C but the decrease is likely to be gradual, not abrupt. Random embryo formation of course also contributes to that fact.

We think the framework presented actually supports this extreme example the referee has provided. Puddles on soil are an example of water exposed to a very large surface area. Even if we ignore the high chance of very strong nucleators existing (such as biological INP) a $\bar{g}$ distribution retrieved for a soil sample would be enough to explain the freezing happening at such a high temperature because of the very high surface area. So we agree that this is an example that goes counter to the notion that critical contact angle cutoffs exist and hope our concepts are better presented in the revised manuscript.

Response to Referee 2

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.

We thank the referee for their extensive and thoughtful comments. They have helped us significantly improve the content of our manuscript as well as the clarity of the message we wish to convey. We have replied to each comment below and revised the manuscript to address the many questions and concerns raised and improved the clarity of the information being communicated.

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.

We recognize that the original version of our manuscript had been too hasty at times in its assertions about the many concepts presented being physical. In the revised manuscript we have strived to reword much of the content to emphasize that the model presented regarding heterogeneous ice nucleation is a mathematical tool to help describe and interpret the data and derive potentially useful parameterizations. It is not a physical model.

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 _-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 _-PDF and the SBM are continuous in a mathematically sense.

The alpha-PDF and SBM models are similar to our *g* distribution in that they also entail a distribution of active sites. The alpha-PDF model assigns a single contact angle to every particle in a population via a prescribed distribution while the SBM model partitions a particle into discrete active sites and assigns these sites contact angles based on a prescribed distribution. The *g* distribution is closer to the SBM model with the difference being that *the* g framework does not require partitioning a particle into discrete sites but assuming a continuum of activity.
The text has been revised accordingly, on Page/Line 23/6-22:

“There are other formulations that hypothesize an active site based or multi-component stochastic model such as the ones described in Vali & Stransbury (1966), Niedermeier et al. (2011), Wheeler and Bertram (2012), and Wright and Petters (2013). Vali and Stransbury (1966) were the first to recognize that ice nucleating surfaces are diverse and stochastic and thus active sites need to be assigned both a characteristic freezing temperature as well as fluctuations around that temperature. Niedermerier et al. (2011) proposed the soccer ball model, in which a surface is partitioned into discrete active sites with each site conforming to classical nucleating theory. Marcolli et al. (2007) found a Gaussian distribution of contact angles could best describe their heterogeneous ice nucleation data in a completely deterministic framework. Welti et al. (2012) introduced the alpha-PDF model where a probability density function prescribes the distribution of contact angles that a particle population possesses, such that each particle is characterized by a single contact angle. Wright and Petters (2013) hypothesized the existence of a Gaussian probability density function for a specific species, which in essence is similar to the $\bar{g}$ framework described here. The notable difference is that this probability density function was retrieved via optimizing for all freezing curves, and not independently fitting high concentration freezing curves as we have done here.”

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.

Presentation of details about the sampling model has been improved in the manuscript and we hope it is now clearer (more information on this is discussed below). The text has been revised on Page/Line 17/6-26:

“To predict the freezing curves of the droplets with particle surface areas lower than the estimated critical area for the systems considered here, the aggregate surface area of the entire particle population within each droplet is modeled as one large surface. A contact angle θ_r is randomly selected from the full contact angle range [0, π], and the value of active site distribution g^* for the particle *i* being sampled for at θ_r is assigned the value of $\overline{g(\theta_r)}$:

$$\left(g_i^*(\theta_{r,n_{draw}})\right) = \overline{g(\theta_r)} \qquad (16)$$

The g distributions within this numerical model are given an asterix to indicate that they are discrete distributions.

This process is repeated for a parameter n_{draws}, for each droplet in the array that produced the freezing curve being modeled. n_{draws} is the only parameter that is optimized for so the modeled freezing curves can predict the behavior of the experimental freezing curves. The value of n_{draws} typically ranges from 9 to 65 for the systems analyzed here and is therefore a relatively soft optimization parameter with small dynamic range. The sampled g^* distributions are normalized with respect to the estimated total surface area for the freezing curve being modeled before being used to compute the freezing probability. Using the sampled g distributions the freezing probability of each droplet is calculated using Eq. (9) and the frozen fraction curve is computed from the arithmetic average of the freezing probabilities:

$$F(below\ critical\ area) = \frac{1}{N}\sum_{i=1}^{N} P_{f_i} \qquad (17)$$

where N is the number of droplets in the cold plate array."

We have removed previous assertions of discovering something "real" with the model being able to fit the data. While the number of draws is just another fit parameter, it actually turns out to be a fairly "soft" optimization parameter varying from 9 to 65 for all the systems considered (additional datasets beyond illite are now analyzed). We hope that the new details and analysis provided will add to the clarity of this aspect of the paper.

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 theta is randomly chosen but does this mean that theta is first sampled from a uniform probability density function, and then g(theta) 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 theta 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?

We now explain these details below and in the revised manuscript. A contact angle is first randomly drawn from the full contact angle range. After which the value of the g distribution being modeled at that contact angle is assigned the value of $\bar{g}$ at that randomly drawn contact angle. The process is repeated for n_{draws}. After a few repetitions (on the order of 20 for the illite and cellulose distributions, for example) the sampled g distribution will mimic $\bar{g}$. So one can say that the method does also work for modeling curves above the critical area threshold.
The text has been revised on Page/Line 18/5-8:
"It should also be noted that there is an n_{draws} value for each system above for which the sampled distribution mimics $\bar{g}$. For example, when n_{draws} is 25 for the Illite system the retrieved distribution will produce a freezing curve equivalent to using $\bar{g}$."

The manuscript does not sufficiently discuss previous work on immersion freezing. On the model side, the authors could test if "subsampling" of an _-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.

We do recognize that a different version of the sampling model can be built around an already existing scheme like n_s. We point to some of the similarities between $\bar{g}$ and n_s in that we think they both represent active site distribution for particle surfaces above the defined critical area. We also do recognize (and have added emphasis on this in the revised manuscript) that is not the first approach to successfully fit frozen fraction curves for illite for other systems. It is just, as the reviewer points out, different and offers what we think are some valuable insights on how heterogonous ice nucleation datasets may be exhibiting a surface area dependence that hasn't been traditionally accounted for. Our new compilation of more illite data and its comparison with the previously reported n_s values from different measuring techniques should add value to the manuscript and clarify this message.

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 _m 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 the revised manuscript we present additional datasets for illite, cellulose, and Snomax that exhibit a similar trend with decreasing surface area as the Broadley et al. data to make a stronger case for the value of this dependence on surface area and what we think it entails. We agree that there is a surface area uncertainty for any of the freezing curves and acknowledge that it partly may contribute to some of the broadness in the freezing curves. However, this uncertainty would not explain a consistent trend with decreasing surface area but would create a margin of error in temperature over which the freezing curve can lie.

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.

The words "consistent and comprehensive" have been removed and replaced with "well established". We just want to emphasize that the community has yet to settle on one standard way to describe and report heterogeneous ice nucleation properties.

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?

We have removed the reference to internal and external variability in the abstract. It is now introduced and defined later in the text.

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

We have removed all references to "statistically significant" in the revised manuscript to avoid misrepresenting the framework and its interpretation of the data.

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.

This sentence has been removed from the abstract. When this conclusion is made later in the paper, we have made sure to indicate that the result is based on our model and not a physical reality.

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).

This has been reworded to say that based on the model presented by Vali (2008), the experimental results are suggestive of active sites on preferential locations, on Page/Line 3/19-20: "These results suggest that there is a strong spatial preference on where nucleation occurs, supporting a model of discrete active sites."

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.

Time dependence is only addressed briefly to introduce the framework and doesn't comprise an essential element of the message the paper is trying to convey. Our understanding of the current state of knowledge is that heterogeneous ice nucleation is much more strongly dependent on temperature than time (Vali, 2014; Wright and Petters, 2013). As stated in the manuscript, whether the role of time has proven to not merit inclusion in models remains to be seen. It is with our understanding of its potential importance that we have developed our framework to still account for time despite time dependent analysis not being a major focus in this work where we focus on the surface area dependence.

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

This is a typo. "Completely" should be followed by "discarded". This has been corrected.

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?

We have reworded the text here to avoid general statements and merely indicate an important finding of Ervens and Feingold (2012). Text has been revised on page/line 4/1-7:
"Ervens and Feingold (2012) tested different nucleation schemes in an adiabatic parcel model and found that critical cloud features such as the initiation of the WBF process, liquid water content, and ice water content, all diverged for the different ice nucleation parameterizations. This strongly affected cloud evolution and lifetime. The divergence was even stronger when the aerosol size distribution was switched from monodisperse to polydisperse."

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.

"First principles of classical nucleation theory" has been changed to "based on classical nucleation theory".

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.

We have reworded this to emphasize that internal and external variability along with the other concepts presented here are modeling tools to describe and interpret the data and present a means to model ice nucleation behavior. They are not physical realities in the strict sense. We have revised the text, on Page/Line 4/11-15:
"The new framework is stochastic by nature to properly reflect the randomness of ice embryo growth and dissolution, and assumes that an ice nucleating particle can exhibit variability in active sites along its surface, what will be referred to as internal variability, and variability in active sites between other particles of the same species, what will be referred to as external variability."

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.

Interpret has been changed to "describe".

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.

The text has been changed to indicate that the stochastic formulation is one that uses CNT with a single contact angle assumption and not that CNT assumes embryo formation is uniform over the surface considered. On Page/Line 6/3-4:
"The simplest stochastic formulation hypothesizes that the nucleation rate is uniform across the ice nucleating particle's surface, i.e. makes a single contact angle assumption."

We have also omitted the reference to CNT on p. 8, l. 12-14:
"The single θ fit has a steeper dependence on temperature a result of the double exponential temperature dependence of the freezing probability in Eq. (4) (J is an exponential function of temperature in itself as can be seen in Eq. (2)) results in an approximately temperature step function."

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.

It is now indicated that every particle is assumed to have the same surface area A in the derivation of equation (3), on Page/Line 6/10-11:
" A is the surface area of each individual ice nucleating particle (assumed to be the same for all particles)."

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

The text has been modified on Page/Line 6/17-20:
"Given the large variability in particle surface composition and structure across any one particle, which in turn determines the activity (or contact angle, θ) of a potential ice nucleating site, a different approach is to assume that the heterogonous nucleation rate will vary along the particle-droplet interface."

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.

We have placed emphasis on the concepts of internal and external variability being introduced in this manuscript as part of a new framework.

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.

"Direct insight" has been omitted.

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.

The symbol for time t has been replaced with $T(t)$ in the parentheses following J since it is temperature that is a function of time and not J.

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.

We have reworded the text here to indicate that internal variability and its impact on time dependence is a mathematical model of what is happening and not a physical interpretation. The claim that evidence of internal variability is captured is discarded. The text was revised on Page/Line 9/11-14:
"The diversity of nucleating ability on the particle surface captured by the g parameter offsets some of the steepness and yields a more gradual freezing curve, more similar to the actual experimental freezing probability curve."

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.

We have attempted to better describe the details of the modeling exercise done here. We actually run equation (7) for all temperatures for a constant time of 1 hour to assess the freezing probability that results from the hypothetical g distribution retrieved under different conditions. The dotted red line is the modeled freezing probability of the droplets for all temperatures after a waiting time of 1 hour. The text was revised on Page/Line 9/15-23:
"Two droplet freezing probability fits (dotted lines) are also plotted in Fig. 1 under different environmental conditions. Instead of prescribing a cooling rate the freezing probabilities are generated by running Eq. (7) for the entire temperature range with each fit for Δt = 1 hour. One fit uses the same g distribution used previously, while the additional single θ fit is approximated as a normal distribution with a near zero standard deviation, similar to a Delta Dirac function. The resultant freezing probabilities are then computed and plotted for every T. It can be seen that the g fit retains much stronger time dependence, with the freezing probability curve shifting about 5 K warmer and the single θ curve shifting just 1 K warmer for the 1 hour hold time."

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 parameterizations have also been able to describe ...". I assume the authors want to put out this new idea, something to further investigate in the future...

We have added references to similar modeling exercises that have been reported and experimental data showing a stronger role of time than a single theta fit would project. The conclusion of this section has been reworded to emphasize that a multiple theta fit does a better job of fitting the experimental data, be it caused by the broadness in a single droplet's freezing probability curve or the effect of time on freezing. The text was revised on Page/Line 9/24-27 and 10/1-14:
"Wider *g* distributions therefore yield stronger time dependence due to the partial offset of the strong temperature dependence that the nucleation rate in Eq. (2) exhibits. The result emphasizes that how the active sites are modeled has consequences on what physical parameters (e.g. time, temperature, cooling rate) can influence the freezing outcome and observed droplet freezing temperature spectrum (Broadley et al., 2012). In Fig. 1 a wider *g* distribution resulted in higher sensitivity to time, which resulted in a shift of the freezing curve to higher temperatures as the system was allowed to temporally evolve at a fixed temperature. This significant change in the freezing probability's sensitivity to temperature is the cause of the more gradual rise in the freezing probability for the system when applying a non-Delta Dirac *g* distribution. This is effectively enhancing the stochastic element in the particle's ice nucleation properties. The shallower response of freezing probability to decreasing temperature (deterministic freezing) creates a greater opportunity for time-dependent (stochastic freezing) to manifest, as a larger fraction of the droplets spend more time unfrozen. The enhancement of the stochastic element brings about a more important role for time as shown in Fig. 1. The finding of this exercise is consistent with previously published work on time dependent freezing such as those reported by Barahona (2012), Vali and Stransbury (1966), Vali (1994b), and Wright and Petters (2013), amongst others."

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)?

In the n_draws method, even though a random contact angle is drawn from a uniform distribution (no preference as to where in the contact angle range of 0 to 180 it is drawn from) the value of *g* for the particle is then assigned the value of g_bar at the random contact angle value chosen. Once all the random draws are made, the new resultant discrete probability distribution is created from the contact angles sampled from g_bar, and this is then weighted by the surface area of the particle being modeled. This results in a bias for contact angles with higher g_bar values to be represented. Further clarification of the procedure has been added to the text on Page/Line 16/29-30 and 17/1-16 along with a new figure (bottom of Figure 4) that displays a schematic showing the details of this procedure:

"To predict the freezing curves of the droplets with particle surface areas lower than the estimated critical area for the systems considered here, the aggregate surface area of the entire particle population within each droplet is modeled as one large surface. A contact angle θ_r is randomly selected from the full contact angle range [0, π], and the value of active site distribution g^* for the particle *i* being sampled for at θ_r is assigned the value of $\overline{g(\theta_r)}$:

$$\left(g_i^*(\theta_{r,n_{draw}})\right) = \overline{g(\theta_r)} \qquad (16)$$

The g distributions within this numerical model are given an asterix to indicate that they are discrete distributions.

This process is repeated for a parameter n_{draws}, for each droplet in the array that produced the freezing curve being modeled. n_{draws} is the only parameter that is optimized for so the modeled freezing curves can predict the behavior of the experimental freezing curves. The value of n_{draws} typically ranges from 9 to 65 for the systems analyzed here and is therefore a relatively soft optimization parameter with small dynamic range. The sampled g^* distributions are normalized with respect to the estimated total surface area for the freezing curve being modeled before being used to compute the freezing probability. The bottom part of Figure 4 shows a schematic of how g^* is retrieved from $\overline{\square}$ using n_{draws}."

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.

We have changed the description here and we are no longer referring to the ice nucleating spectrum as one site. It is now referred to as a spectrum of ice nucleating activity, comprised of many sites with strengths and frequencies determined by the Gaussian *g* distribution. Emphasis on the ascending part of this distribution is given since it is the fraction of the curve that determines the modeled freezing probability. The text has been revised on Page/Line 10/25-29:
"It is therefore sufficient to conceptualize that the particle has a well-defined monotonic spectrum of active sites increasing in frequency while decreasing in strength. The spectrum is modeled as a continuum of ice nucleation activity described by the *g* distribution, as depicted on the upper right hand corner in Fig. 2."

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.

We have added a plot showing the *g* distribution used here and indicated the part of the distribution covered in by the critical contact angle range on the plot. It has been added to Figure 3.

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.

The estimate of the ice nucleation area provided by this analysis provides useful information that can be compared to other estimates of this quantity, as we have done in the paper. We have revised the text to clarify that this does not provide a direct measurement of the active site size, on Page/Line 12/1-12:

"Furthermore, the critical contact angle range can be used to estimate a hypothetical nucleating area of the particle – the total active site surface area where nucleation will take place. The nucleation area $A_{nucleation}$ can be estimated as follows:

$$A_{nucleation} = A \int_{\theta_{c_1}}^{\theta_{c_2}} g(\theta) d\theta \qquad (11)$$

For the large ash particle system analyzed in the previous section (Fig. 1) it is estimated that $\theta_{c1} \approx 0.4$ rad and $\theta_{c2} \approx 0.79$ rad. Application of Eq. (11) yields a total ice active surface area estimate of 27 nm^2. Classical nucleation theory estimates that the area of a single active site is 6 nm^2 (Lüönd et al., 2010; Marcolli et al., 2007). The estimated total area of nucleation is therefore consistent with this value and supports the argument that competition between sites along the critical range of θ is taking place. However, the surface area where ice nucleation is occurring remains a very tiny fraction of the total particle surface."

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 micrometersized 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.

To our knowledge, there isn't a cold plate technique that probes single atmospherically relevant sized particles per droplet. Since cold plate droplets arrays are prepared from particle suspensions, an experiment in which atmospherically relevant particle surfaces areas (particle count per droplet will still be high) can be conducted. The manuscript does not intend to show that using large particles results in erroneous nucleation descriptions but that there is a particle surface area dependence of ice nucleation beyond the scaling factor used in both the n_s and CNT based schemes. We show evidence of this in our retrievals of n_s directly from the experiments, whereby at low surface area n_s values retrieved from cold plate methods do not overlap in temperature space. The model presented is a mathematical tool that attempts to describe why droplets containing particles with large total surface areas freeze more uniformly than droplets with small surface areas do, for the datasets considered here. We feel that the new datasets added to the manuscript and their discussion demonstrate this variability in n_s as particle concentration and thus surface area is varied.

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.

When considering droplets with many particles immersed in them we consider the sum of all individual particle surfaces as one surface area of interest. So when we try to describe these datasets in the context of our framework we treat the immersion as one particle, of which its surface area is estimated using the measured surface area density of the studied sample. We have

clarified this in the revised text, on Page/Line 13/5-7:
"For the application of this model to cold plate data where droplets are prepared from a suspension of the species being investigated, the particle population in each droplet is treated as one aggregate surface."

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

We have removed all references to "statistical significance" previously included. Please see our reply to your comment above.

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.

The use of the term "system" was not consistent in the original manuscript as it referred to both an individual droplet at points and to a species being investigated at other points. The word system now refers to the species under consideration, e.g.. illite particles, and it is not used to describe a droplet in the earlier equation derivations.

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

We have worked to change the text to suggest that the results are to be interpreted in the context of the mathematical model presented and not in the absolute physical sense. The text was revised on Page/Line 14/7-15:
"Above a certain surface area threshold it is conceptualized that the chance of an ice-nucleating particle surface not possessing the entire range of ice nucleating activity (θ) becomes very small. The model therefore assumes that any particle or ensemble of particles having a total surface area larger than the critical area can be approximated as having $\bar{g}$ describe the actual g distribution of the individual particles. In other words, for large particles with more surface area than the critical area threshold, it is assumed that the external variability between individual particles will be very small such that the particle population can just be described by one average continuous distribution of the ice active site ability, $\bar{g}$."

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

Removed, please see above.

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?

High particle concentrations are a reference to concentrations that result in total particle surface areas in the droplet greater than the critical area threshold we have identified for that particle system. The structure of this entire section has been changed significantly to make the presentation of the results and the model clearer. The retrieved average g distribution is the g

distribution that creates the best fit of the data using Equation (9). Stating "average" before "g distribution" is unnecessary and misleading and has thus been omitted. The text has been revised thoroughly, on Page/Line 14/16-26:

"To resolve the g distributions of the systems possessing particle surface areas smaller than the critical area the first step is to approximate the critical area. Experiments must start at very high particle surface area concentrations to ensure the number of particles and total surface area per droplet exceeds the critical area. For the illite mineral particle case study considered next, for example, high particle concentrations were those that resulted in total particle surface areas greater than about 2×10^{-6} cm^2. The particle number or surface area concentration is then decreased until the retrieved g distribution (from the measured droplet freezing temperature spectrum for an array of droplets containing particles) can no longer be reasonably predicted by $\bar{g}$. This point can identify the parameter A_c, the critical area of the species under study. A schematic of the procedure is summarized in Fig. 4."

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.

As mentioned in the previous response, much of the organization of this section has been improved, in part to address the referee's suggestions.

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.

In this part of the text we were referring to the success of the n_s scheme in describing the freezing behavior for the high particle surface area experiments. We were not referring to the results of the presented model yet. We hope that the format of the new section will clarify many of this unintentionally misrepresented issues.

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?

New datasets retrieved with our own cold plate system using illite NX, Snomax, and cellulose particle systems and their analysis have been added to the manuscript.

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?

A running index i for $g^*(\theta_r)$ has been added to indicate the nth droplet being modeled. An additional index for θ_r has also been added to indicate what the n_{draw} it is being used for.

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...?*

The values of n_{draws} for each dataset analyzed in the revised manuscript have been added to the text. The values actually vary from 9 to 65 for all the 3 systems studied here (illite, Snomax, cellulose). A random contact angle is first chosen from the entire contact angle range. Because of the nature of the sampling process, a large number of draws is not necessary for sampling from the very active contact angle range. When a random contact angle is selected, its value at *g*_bar is assigned to the *g* distribution being generated at that same contact angle. The number of draws required to generate a *g* distribution similar to *g*_bar ends up being on the order of 25 for the cellulose and illite, and about 70 for Snomax, because enough contact angles have been selected to approximate g_bar. Note that a new $g*$ distribution is created using n_draws for each droplet for that system. The freezing probability for each droplet in the array is calculated using the new sub-sampled $g*$ distribution, and Eq. (9). This is followed by using Eq. (17) to compute the modeled frozen fraction. The confusing regarding this method is understandable, and we have revised the text to clarify this, on Page/Line 16/29-30 and 17/1-16:

"To predict the freezing curves of the droplets with particle surface areas lower than the estimated critical area for the systems considered here, the aggregate surface area of the entire particle population within each droplet is modeled as one large surface. A contact angle θ_r is randomly selected from the full contact angle range [0, π], and the value of active site distribution g^* for the particle *i* being sampled for at θ_r is assigned the value of $\overline{g(\theta_r)}$:

$$\left(g_i^*(\theta_{r,n_{draw}})\right) = \overline{g(\theta_r)} \qquad (16)$$

The g distributions within this numerical model are given an asterix to indicate that they are discrete distributions.

This process is repeated for a parameter n_{draws}, for each droplet in the array that produced the freezing curve being modeled. n_{draws} is the only parameter that is optimized for so the modeled freezing curves can predict the behavior of the experimental freezing curves. The value of n_{draws} typically ranges from 9 to 65 for the systems analyzed here and is therefore a relatively soft optimization parameter with small dynamic range. The sampled g^* distributions are normalized with respect to the estimated total surface area for the freezing curve being modeled before being used to compute the freezing probability. The bottom part of Fig. 4 shows a schematic of how g^* is retrieved from $\bar{g}$ using $n_{draws.}$ With the sampled g^* distributions the freezing probability of each droplet is calculated using Eq. (9) and the frozen fraction curve is computed from the arithmetic average of the freezing probabilities:

$$F(below\ critical\ area) = \frac{1}{N}\sum_{i=1}^{N} P_{f_i} \qquad (17)$$

where N is the number of droplets in the cold plate array."

The values of n_{draws} for all systems modeled are now reported on Page/Line 17/24-28:

"The values of n_{draws} for the lower concentration freezing curves for each of the systems investigated here are 21 (2.02×10^{-6} cm^2), 19 (1.04×10^{-6} cm^2), and 11 (7.11×10^{-7} cm^2) for the droplets containing illite; 65 (0.09 wt%), 48 (0.08 wt%), and 23 (0.07 wt%) for the droplets containing Snomax; and 21 (0.05 wt%), 11 (0.01 wt%), and 9 (0.001 wt%) for the droplets containing cellulose."

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

We recognize that uncertainty in surface area could result in a significant difference in the predicted temperature range over which freezing would occur for droplets studied here. However, this uncertainty would not explain the consistent trend of broader freezing temperatures as surface area decreases unless surface area uncertainties became larger with decreasing concentration. We do not see why surface area uncertainty would increase with decreasing concentration; in fact we think the opposite is true where at high concentrations the suspensions become less stable due to potential particle coagulation and settling. Physical artifacts under high particle concentrations that lead to coagulation and settling are now discussed in the text for the illite measurements.

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?

Much of the wording of this section has already been changed in an attempt to clarify the implications of the analysis done. The use of "qualitative" and "quantitative" was unnecessary here. We were simply trying to emphasize that the presented model is able to describe the trend seen in the freezing curves as the surface area of the particles is lowered. We have revised the text, on Page/Line 17/16-21:
"The behavior of the experimental curve is captured using the n_{draws} numerical model in which random sampling from the ice nucleating spectrum dictated by $\bar{g}$ is carried out to predict the freezing curve. The dotted lines in Figs. 5, 6, and 7 are obtained by sampling from the $\bar{g}$ model to successfully predict the behavior of all the freezing curves. The early freezing onsets of the lower concentration systems as well as the broadness in the curves are both captured with the model."

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

The division of the particle into tiny patches is actually not part of the model presented, but that of an alternative model that is still being developed. We have omitted this sentence.

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.

The revised manuscript stresses that this is a hypothesis and a suggestive mathematical description of the observations. We have removed assertions of a physical reality. We have revised the text accordingly, on Page/Line 18/1-18:

"Perhaps the most notable characteristic is how these freezing curves ascend together early as temperature is decreased but then diverge as the temperature decreases further. The closeness of the data at warmer temperatures (the ascent) is interpreted by the framework as the presence of some rare high activity active sites within the particle population under all the particle concentrations explored in these experiments. At lower temperatures it appears that there is a wider diversity in the activity of droplets that did not contain these rare efficient active sites, and thus there is significant spread in the freezing curve for $T < 242$ K. In the context of the framework presented here this can be attributable to strong external variability of the ice nucleating population, with very strong/active nucleators causing similar freezing onsets for different particle concentrations at the warmer temperatures, and a lack of strong nucleators explaining the less consistent freezing of the unfrozen droplets at lower temperature. Thus it follows that there is a wider spread in the freezing curves for these droplets, as their freezing temperature is highly sensitive to the presence of moderately strong active sites. This expresses a greater diversity in external variability – the active site density possessed by individual particles from the same particle source. In a later section the claim of more external variability contributing to the broader curves below the critical area threshold is supported with a closer look at the numerical results from the model."

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

This has been changed to state that this is the first study that models the process in such a manner.

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.

We do not mean to claim that our method is superior. We were pointing to the difference between using one distribution to describe the freezing data (by drawing from said distribution) and fitting every freezing curve to an independent distribution. The latter approach is treating every freezing curve independently, where the particles in the droplets in the different cases have different active site distributions that are not generated from the same source. We have revised the text accordingly, on Page/Line 22/18-22:
"A similar conclusion along these lines was reached by Broadley et al. (2012) when the authors noted that the best fits to their freezing curves were achieved when the system was assumed to be totally externally variable. That is when each particle was assumed to have a single contact angle but a distribution assigned a spectrum of contact angles to the particle population."

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.

The tone has been modified here to establish the difference between each methods' approach and not a comparison in the value of each method. We have revised the text accordingly, on Page/Line 23/6-22:

"There are other formulations that hypothesize an active site based or multi-component stochastic model such as the ones described in Vali & Stransbury (1966), Niedermeier et al. (2011), Wheeler and Bertram (2012), and Wright and Petters (2013). Vali and Stransbury (1966) were the first to recognize that ice nucleating surfaces are diverse and stochastic and thus active sites need to be assigned both a characteristic freezing temperature as well as fluctuations around that temperature. Niedermerier et al. (2011) proposed the soccer ball model, in which a surface is partitioned into discrete active sites with each site conforming to classical nucleating theory. Marcolli et al. (2007) found a Gaussian distribution of contact angles could best describe their heterogeneous ice nucleation data in a completely deterministic framework. Welti et al. (2012)

introduced the alpha-PDF model where a probability density function prescribes the distribution of contact angles that a particle population possesses, such that each particle is characterized by a single contact angle. Wright and Petters (2013) hypothesized the existence of a Gaussian probability density function for a specific species, which in essence is similar to the $\bar{g}$ framework described here. The notable difference is that their probability density function was retrieved via optimizing for all freezing curves, and not independently fitting high concentration freezing curves as we have done here."

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.

Multi-component here refers to any formulation that assumes multiple active sites. No one heterogeneous ice nucleation parameterization has thus far succeeded in being a standalone standard, and we have changed the text to reflect this. We think there is a general preference to reporting results from different ice nucleation methods for easy comparison using the n_s framework due to its simplicity and ease of use, but not that this formulation is undisputed and the only one to be used to report heterogeneous ice nucleation results. We have revised the text accordingly, on Page/Line 23/23-28:
" The n_s scheme is now more commonly used to describe and compare cold plate and other experimental ice nucleation data over multi-component stochastic formulations (Hiranuma et al., 2015; Murray et al., 2012; Wex et al., 2015). This is in part due to the necessary inclusion of more variables required by other frameworks (such as prescribing a discrete number of active sites in the soccer ball model by Niedermeier et al. (2011)) than the simpler purely deterministic scheme of n_s."

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?

We acknowledge that some computation is required to retrieve frozen fraction curves or freezing probabilities below the critical area. However, this process only needs to be done once, after which the h correction factor can be used to transform the frozen fraction functions below the critical area. We have removed the sentence about this step being computationally cumbersome, as after some consideration we have realized that it shouldn't be considered such.

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.

We agree. The word "trivially" has been removed.

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.

This conclusion along with others about the nature of the active site distribution on particles below and above the critical area, are meant to be stated in the context of the model presented and not as physical realties. We hope that the changes throughout the manuscript on this general issue will correct this shortcoming and clarify our meaning.

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.

We have changed this to state that more studies need to be performed to determine if atmospherically relevant particles exhibit the same trend examined in this paper. We have revised the text accordingly, on Page/Line 26/10-12:
"More detailed analysis studying various atmospherically relevant ice nucleating particles needs to be done to shed light on whether a particle size cutoff corresponding to a critical area threshold can be used to describe the behavior of different species."

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

We have changed the tone of this statement to indicate that our findings point to one n_s parameterization not being sufficient to describe all illite ice nucleation behavior, as we have seen the values of this function do not overlap at lower surface areas. Variation in n_s for illite NX was also reported and extensively discussed by Hiranuma et al. (2014). Perhaps one n_s function may be sufficient, but some form of a correction might be needed at low surface areas where we think the actual active site density becomes different between sample surfaces contained in individual droplets.

The crux of our argument is that the surface area normalization assumption that underlies the n_s framework warrants closer inspection and evaluation. The ice nucleation community has essentially been operating under the assumption that the same n_s value will always be retrieved from any proper method, regardless of how large a difference in particle concentration or surface area exists between methods. Inconsistencies in the n_s values retrieved using different methods for the same system (such as illite NX and cellulose MCC) are widely known and discussed in the community. This is often thought to be caused by differences between the methods used, and their method artifacts. Particle coagulation and settling at high particle concentrations is one proposed method artifact, which we also suspect explains our highest concentration illite data. We are suggesting that the observed difference in n_s between methods and research groups may be more fundamental in nature and caused by changes in the distribution of active sites contained in particles sampled in the individual droplets that compose the arrays used in cold plate methods. We have presented experimental data from three systems and two research groups that demonstrate this variability in n_s as particle concentration and surface area are changed, and used our model to interpret and propose an explanation for these effects. While we agree we have not conclusively proven that our interpretation of the causes of these changes in n_s is the correct answer, we do not believe that there is available evidence that disproves our hypotheses. Considering the ongoing issues in reliably determining the concentration of INP and their ice nucleation properties/activity, a healthy debate that considers many possible explanations is warranted. This proposal is the main intent of our central hypothesis and the supporting data and analysis presented. Our discussion of the n_s framework has been revised in the text, and data from our cold plate system for Snomax, illite, and cellulose has been added to the revised paper.

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.

The intention of this paragraph is to state that the cold plate technique enables probing a large surface area range which aids in determining whether a single active site density function is sufficient to describe data for all size of a considered particle species or not. Tone has been changed to sound less assertive and more suggestive, on Page/Line 27/4-12:

"Cold plate experimental data potentially provides sufficient information to describe heterogeneous ice nucleation properties in cloud parcel and atmospheric models, however the analysis undertaken here suggests that retrieving one active site density (i.e. n_s) parameterization and applying it to all surface areas can result in misrepresenting the freezing behavior. When samples are investigated, probing a wide concentration range enables the determination of both general active site density functions (e.g. $\bar{g}$) as well as the behavior of the species' under study at concentrations below the critical area threshold. Once this analysis is undertaken more comprehensive parameterizations can be retrieved as will be developed in the next section."

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

For the example cases considered here we show that extrapolating n_s to lower surface area does yield errors in say a cloud parcel model. This is supported by the n_s retrievals for the example systems considered. This is discussed in the text, please see comment that follows.

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

If a cloud parcel model uses n_s values extrapolated from the high surface area freezing curves for the low surface area freezing curves for the example systems considered, the model will neither capture the onset of freezing nor the range of temperatures over which freezing occurs. We have clarified what we are trying to state here, on Page/Line 27/13-30 and 28/1-2:

"The critical area analysis carried out in this paper emphasizes the dangers in extrapolating the freezing behavior of droplets containing a large concentration of particle to droplets containing smaller concentrations or individual particles. Applying a parameterization such as n_s directly to systems below the critical area threshold in a cloud parcel model for example yields large differences in the predictions of the freezing outcome of the droplet population. As the concentration of the species within the droplets was decreased in the cold plate freezing spectra considered here the actual freezing temperature curves diverged more and more from those predicted when the systems were assumed to be above the critical area. This led to significant changes in the retrieved n_s values, as shown in Figs. 4b, 6b, and 7b. The large effects of concentration on the droplet freezing temperature can be directly observed in the frozen fraction curves plotted in Figs. 5, 6a, and 7a. Differences between observed frozen fraction curves and ones that assumed uniform active site density yielded errors in the temperature range the droplets froze over as well as the temperature at which 50% frozen fraction point. Therefore, a cloud parcel model would be unable to accurately predict the freezing onset or the temperature range over which freezing occurs using a single n_s curve obtained from high concentration data. This has important consequences for the accurate simulation of the microphysical evolution of the cloud system under study such as the initiation of the Wegener–Bergeron–Findeisen and the consequent glaciation and precipitation rates (Ervens and Feingold, 2012; Ervens et al., 2011)."

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.

We have incorporated the suggestions of both referees to shorten, reorganize, and clarify the final section and Conclusions of the paper, and appreciate the referee's feedback. This section now read as follows, on Page/Line 27/13-30:

"The critical area analysis carried out in this paper emphasizes the dangers in extrapolating the freezing behavior of droplets containing a large concentration of particles to droplets containing smaller concentrations. Applying a parameterization such as n_s directly to systems below the critical area threshold in a cloud parcel model for example yields large differences in the predictions of the freezing outcome of the droplet population. As the concentration of the species within the droplets was decreased in the cold plate freezing spectra considered here the actual freezing temperature curves diverged more and more from those predicted when the systems were assumed to be above the critical area. This led to significant changes in the retrieved n_s values, as shown in Figs. 4, 6b, and 7b. The large effects of concentration on the droplet freezing temperature can be directly observed in the frozen fraction curves plotted in Figs. 5, 6a, and 7a. Differences between observed frozen fraction curves and ones that assumed uniform active site density yielded errors in the temperature range the droplets froze over as well as the median droplet freezing temperature. Therefore, a cloud parcel model would be unable to accurately predict the freezing onset or the temperature range over which freezing occurs using a single n_s curve obtained from high concentration data. This has important consequences for the accurate simulation of the microphysical evolution of the cloud system under study such as the initiation of the Wegener–Bergeron–Findeisen and the consequent glaciation and precipitation rates (Ervens and Feingold, 2012; Ervens et al., 2011)."

We revised and moved one of the paragraphs from this section to the Conclusions. The revised Conclusions are now as follows:

"Cold plate droplet freezing spectra were carefully examined to investigate a surface area dependence of ice nucleation ability whereby one active site density function such as n_s cannot be extrapolated from high particle surface area to low particle surface area conditions. A method based on the notion of a critical surface area threshold was presented. It is argued that a species' entire ice nucleating spectrum can be confined within a global probability density function $\bar{g}$. For a system, be it one particle or an ensemble of particles, to have a total surface area greater than the critical area is a question of whether the surface is large enough to express all the variability in that particle species' ice active surface site ability. By analyzing droplets containing illite minerals, MCC cellulose, and commercial Snomax bacterial particles, it was shown that freezing curves above a certain critical surface area threshold could be predicted directly from the global $\bar{g}$ distribution obtained from the high particle concentration data alone. The lower particle concentration freezing curves were accurately predicted by randomly sampling active site abilities (θ) from $\bar{g}$ and averaging their resultant freezing probabilities. This framework provides a new method for extrapolating droplet freezing temperature spectra from cold plate experimental data under high particle concentrations to atmospherically realistic dilute particle-droplet systems.

We found that the shifts to colder freezing temperatures caused by reducing the particle concentration or total surface area present in droplets cannot be fully accounted for by simply normalizing to the available surface area, as is done in the ice active site density (n_s) analysis framework. When the surface area is below the critical area threshold the retrieved values of n_s can increase significantly for the same particle species as the particle concentration is decreased. Above the critical area threshold the same n_s curves are retrieved when particle concentration is changed. Atmospheric cloud droplets typically contain just one particle each. Therefore, this effect of particle concentration on droplet freezing temperature spectra and the retrieved n_s values has important implications for the extrapolation of cold plate droplet freezing measurements to describe the ice nucleation properties of realistic atmospheric particles.

Systems that probe populations of droplets each containing one particle such as the CFDC are unable to probe a large particles-in-droplet concentration range but are powerful tools for the real-time investigations of ice nucleating particles at the realistic individual particle level (DeMott et al., 2010; Sullivan et al., 2010; Welti et al., 2009). The frozen fraction curves produced from such an instrument do not provide enough information to associate the observed variability in ice nucleation ability to internal or external factors. However, future laboratory studies using the critical area cold plate technique we have introduced here (e.g. Fig. 4) will provide new insight into the critical area thresholds of internal variability in ice active site ability for different species. This will produce more informed assumptions regarding the variability in ice nucleation properties observed through online field instruments, specifically when the measurements are made in conjunction with single particle chemical analysis techniques (Creamean et al., 2013; DeMott et al., 2003, 2010; Prather et al., 2013; Worringen et al., 2015).

Atmospherically relevant particle sizes may very well fall below the critical area threshold for an individual particle, at least for some species such as illite mineral particles considered here. Therefore, average ice nucleation spectra or active site distributions such as n_s and $\bar{g}$ may not be applicable for representing the ice nucleation properties of particles in cloud and atmospheric models. However careful examination of the surface area dependence of ice nucleating ability of a species allows more accurate retrievals of active site density distributions that properly encompass this dependence."

Cited References:

Barahona, D.: On the ice nucleation spectrum, Atmos. Chem. Phys., 12(8), 3733–3752, 2012.

Broadley, S. L., Murray, B. J., Herbert, R. J., Atkinson, J. D., Dobbie, S., Malkin, T. L., Condliffe, E. and Neve, L.: Immersion mode heterogeneous ice nucleation by an illite rich powder representative of atmospheric mineral dust, Atmos. Chem. Phys., 12, 287–307, doi:10.5194/acp-12-287-2012, 2012.

Creamean, J. M., Suski, K. J., Rosenfeld, D., Cazorla, A., DeMott, P. J., Sullivan, R. C., White, A. B., Ralph, F. M., Minnis, P., Comstock, J. M., Tomlinson, J. M. and Prather, K. a: Dust and biological aerosols from the Sahara and Asia influence precipitation in the western U.S., Science, 339(6127), 1572–8, doi:10.1126/science.1227279, 2013.

DeMott, P. J., Cziczo, D. J., Prenni, A. J., Murphy, D. M., Kreidenweis, S. M., Thomson, D. S., Borys, R. and Rogers, D. C.: Measurements of the concentration and composition of nuclei for cirrus formation., Proc. Natl. Acad. Sci. U. S. A., 100(25), 14655–60, doi:10.1073/pnas.2532677100, 2003.

DeMott, P. J., Prenni, A. J., Liu, X., Kreidenweis, S. M., Petters, M. D., Twohy, C. H. and Richardson, M. S.: Predicting global atmospheric ice nuclei distributions and their impacts on climate, PNAS, 107(25), 11217–11222, doi:10.1073/pnas.0910818107, 2010.

Ervens, B. and Feingold, G.: On the representation of immersion and condensation freezing in cloud models using different nucleation schemes, Atmos. Chem. Phys., 12, 5807–5826, doi:10.5194/acp-12-5807-2012, 2012.

Ervens, B., Feingold, G., Sulia, K. and Harrington, J.: The impact of microphysical parameters, ice nucleation mode, and habit growth on the ice/liquid partitioning in mixed-phase Arctic clouds, J. Geophys. Res. Atmos., 116(17), 2011.

Hiranuma, N., Augustin-Bauditz, S., Bingemer, H., Budke, C., Curtius, J., Danielczok, A., Diehl, K., Dreischmeier, K., Ebert, M., Frank, F., Hoffmann, N., Kandler, K., Kiselev, A., Koop, T., Leisner, T., Möhler, O., Nillius, B., Peckhaus, A., Rose, D., Weinbruch, S., Wex, H., Boose, Y., DeMott, P. J., Hader, J. D., Hill, T. C. J., Kanji, Z. A., Kulkarni, G., Levin, E. J. T., McCluskey, C. S., Murakami, M., Murray, B. J., Niedermeier, D., Petters, M. D., O'Sullivan, D., Saito, A., Schill, G. P., Tajiri, T., Tolbert, M. A., Welti, A., Whale, T. F., Wright, T. P. and Yamashita, K.: A comprehensive laboratory study on the immersion freezing behavior of illite NX particles: a comparison of 17 ice nucleation measurement techniques, Atmos. Chem. Phys., 15(5), 2489–2518, doi:10.5194/acp-15-2489-2015, 2015.

Lüönd, F., Stetzer, O., Welti, A. and Lohmann, U.: Experimental study on the ice nucleation ability of size-selected kaolinite particles in the immersion mode, J. Geophys. Res., 115(D14), 2010.

Marcolli, C., Gedamke, S., Peter, T. and Zobrist, B.: Efficiency of immersion mode ice nucleation on surrogates of mineral dust, Atmos. Chem. Phys., 7(19), 5081–5091, 2007.

Murray, B. J., O'Sullivan, D., Atkinson, J. D. and Webb, M. E.: Ice nucleation by particles immersed in supercooled cloud droplets, Chem. Soc. Rev., 41(19), 6519, 2012.

Niedermeier, D., Shaw, R. a., Hartmann, S., Wex, H., Clauss, T., Voigtländer, J. and Stratmann, F.: Heterogeneous ice nucleation: exploring the transition from stochastic to singular freezing behavior, Atmos. Chem. Phys., 11(16), 8767–8775, doi:10.5194/acp-11-8767-2011, 2011.

Prather, K. a, Bertram, T. H., Grassian, V. H., Deane, G. B., Stokes, M. D., Demott, P. J., Aluwihare, L. I., Palenik, B. P., Azam, F., Seinfeld, J. H., Moffet, R. C., Molina, M. J., Cappa, C. D., Geiger, F. M., Roberts, G. C., Russell, L. M., Ault, A. P., Baltrusaitis, J., Collins, D. B., Corrigan, C. E., Cuadra-Rodriguez, L. a, Ebben, C. J., Forestieri, S. D., Guasco, T. L., Hersey, S. P., Kim, M. J., Lambert, W. F., Modini, R. L., Mui, W., Pedler, B. E., Ruppel, M. J., Ryder, O. S., Schoepp, N. G., Sullivan, R. C. and Zhao, D.: Bringing the ocean into the laboratory to probe the chemical complexity of sea spray aerosol., Proc. Natl. Acad. Sci. U. S. A., 110(19), 7550–5, doi:10.1073/pnas.1300262110, 2013.

Sullivan, R. C., Miñambres, L., DeMott, P. J., Prenni, A. J., Carrico, C. M., Levin, E. J. T. and Kreidenweis, S. M.: Chemical processing does not always impair heterogeneous ice nucleation of mineral dust particles, Geophys. Res. Lett., 37(24), n/a–n/a, doi:10.1029/2010GL045540, 2010.

Vali, G.: Freezing Rate Due to Heterogeneous Nucleation, J. Atmos. Sci., 51(13), 1843–1856, 1994.

Vali, G.: Repeatability and randomness in heterogeneous freezing nucleation, Atmos. Chem. Phys., 8(16), 5017–5031, doi:10.5194/acp-8-5017-2008, 2008.

Vali, G.: Interpretation of freezing nucleation experiments: Singular and stochastic; Sites and surfaces, Atmos. Chem. Phys., 14(11), 5271–5294, 2014.

Vali, G. and Stransbury, E. J.: Time Dependant Charactirisitcs of the Heterogeneous Nucleation of Ice, Can. J. Phys., 44(3), 477–502, 1966.

Welti, A., Lund, F., Stetzer, O. and Lohmann, U.: Influence of particle size on the ice nucleating ability of mineral dusts, Atmos. Chem. Phys., 9(18), 6705–6715, 2009.

Welti, A., Luond, F., Kanji, Z. A., Stetzer, O. and Lohmann, U.: Time dependence of immersion freezing : an experimental study on size selected kaolinite particles, , 9893–9907, doi:10.5194/acp-12-9893-2012, 2012.

Wex, H., Augustin-Bauditz, S., Boose, Y., Budke, C., Curtius, J., Diehl, K., Dreyer, a., Frank, F., Hartmann, S., Hiranuma, N., Jantsch, E., Kanji, Z. a., Kiselev, a., Koop, T., Möhler, O., Niedermeier, D., Nillius, B., Rösch, M., Rose, D., Schmidt, C., Steinke, I. and Stratmann, F.: Intercomparing different devices for the investigation of ice nucleating particles using Snomax® as test substance, Atmos. Chem. Phys., 15(3), 1463–1485, doi:10.5194/acp-15-1463-2015, 2015.

Wheeler, M. J. and Bertram, A. K.: Deposition nucleation on mineral dust particles: A case against classical nucleation theory with the assumption of a single contact angle, Atmos. Chem. Phys., 12(2), 1189–1201, doi:10.5194/acp-12-1189-2012, 2012.

Worringen, a., Kandler, K., Benker, N., Dirsch, T., Mertes, S., Schenk, L., Kästner, U., Frank, F., Nillius, B., Bundke, U., Rose, D., Curtius, J., Kupiszewski, P., Weingartner, E., Vochezer, P., Schneider, J., Schmidt, S., Weinbruch, S. and Ebert, M.: Single-particle characterization of ice-nucleating particles and ice particle residuals sampled by three different techniques, Atmos. Chem. Phys., 15(8), 4161–4178, doi:10.5194/acp-15-4161-2015, 2015.

Wright, T. P. and Petters, M. D.: The role of time in heterogeneous freezing nucleation, J. Geophys. Res. Atmos., 118(9), 3731–3743, 2013.

Effect of particle surface area on ice active site densities retrieved from droplet freezing spectra

Hassan Beydoun[1], Michael Polen[1], and Ryan C. Sullivan[1,*]

[1] Center for Atmospheric Particle Studies, Carnegie Mellon University, Pittsburgh PA

Correspondence to: R. C. Sullivan (rsullivan@cmu.edu)

Deleted: **Using critical area analysis to deconvolute internal and external particle variability in heterogeneous ice nucleation** ... [1]

Revised July 12, 2016

Abstract

Heterogeneous ice nucleation remains one of the outstanding problems in cloud physics and atmospheric science. Experimental challenges in properly simulating particle-induced freezing processes under atmospherically relevant conditions have largely contributed to the absence of a well-established parameterization of immersion freezing properties. Here we formulate an ice active surface site based stochastic model of heterogeneous freezing with the unique feature of invoking a continuum assumption on the ice nucleating activity (contact angle) of an aerosol particle's surface, that requires no assumptions about the size or number of active sites. The result is a particle specific property g that defines a distribution of local ice nucleation rates. Upon integration this yields a full freezing probability function for an ice nucleating particle.

Current cold plate droplet freezing measurements provide a valuable and inexpensive resource for studying the freezing properties of many atmospheric aerosol systems. We apply our g framework to explain the observed dependence of the freezing temperature of droplets in a cold plate on the concentration of the particle species investigated. Normalizing to the total particle mass or surface area present to derive the commonly used ice nuclei active surface (INAS) density (n_s) often cannot account for the effects of particle concentration, yet concentration is typically varied to span a wider measureable freezing temperature range. A method based on determining what is denoted an ice nucleating species' specific critical surface area is presented that explains the concentration dependence as a result of increasing the variability in ice nucleating active sites between droplets. By applying this method to experimental droplet freezing data from four different

Deleted: consistent and comprehensive

Deleted: -

Deleted: great

Deleted: statistical significance to determine

Deleted: can resolve the two-dimensional nature of the ice nucleation ability of aerosol particles: *internal*

Deleted: active site strengths and freezing rates along an individual particle's surface, as well as *external* variability

Deleted: two particles of the same type in an aerosol population.

systems we demonstrate its ability to interpret immersion freezing temperature spectra of droplets containing variable particle concentrations.

It is shown that general active site density functions such as the popular n_s parameterization cannot be reliably extrapolated below this critical surface area threshold to describe freezing curves for lower particle surface area concentrations. Freezing curves obtained below this threshold translate to higher n_s values, while the n_s values are essentially the same from curves obtained above the critical area threshold; n_s should remain the same for a system as concentration is varied. However, we can successfully predict the lower concentration freezing curves, which are more atmospherically relevant, through a process of random sampling from *g* distributions obtained from high particle concentration data. Our analysis is applied to cold plate freezing measurements of droplets containing variable concentrations of particles from NX illite minerals, MCC cellulose, and commercial Snomax bacterial particles. Parameterizations that can predict the temporal evolution of the frozen fraction of cloud droplets in larger atmospheric models are also derived from this new framework.

Deleted: comprehensively

Deleted: .

Deleted: the statistically significant global distribution

Deleted: further revealed that one individual atmospheric

Deleted: mineral particle will not contain the entire range of ice active site activity for that system (its internal variability). Comprehensive parameterizations

1 Introduction

Above water's homogenous freezing temperature near -38 °C supercooled cloud droplets can only crystallize on a rare subset of atmospheric aerosol particles termed ice nucleating particles (INP) (Baker and Peter, 2008; Vali et al., 2015). The scarcity of these particles directly affects cloud structure, evolution, and precipitation via inducing the Wegener–Bergeron–Findeisen (WBF) process, where ice crystals rapidly grow at the expense of liquid cloud droplets in mixed-phase clouds. Ice nucleation thus plays a crucial role in determining cloud evolution, lifetime, and properties, creating important feedbacks between aerosols, clouds, precipitation, and climate (Pruppacher & Klett, 1997; Rosenfeld et al., 2008). As a result, most precipitation over land is induced by cloud glaciation (Cantrell and Heymsfield, 2005; Mülmenstädt et al., 2015). Accurate representation of cirrus and mixed phase clouds in atmospheric models therefore necessitates properly parameterizing the heterogeneous ice nucleation process (DeMott et al., 2010; Eidhammer et al., 2009; Hoose et al., 2010; Liu and Penner, 2005) for different aerosol source types and compositions that possess a wide range of heterogeneous ice nucleation activities (Phillips et al., 2008, 2012).

Great challenges in observing the actual heterogeneous ice nucleation nanoscale process is the main culprit impeding the formulation of a consistent and comprehensive framework that can accurately and efficiently represent heterogeneous ice nucleation in atmospheric models (Cantrell and Heymsfield, 2005); we still do not understand what precisely controls the ice nucleation ability of ice active surface sites that catalyze ice embryo formation. There are currently two competing views on the dominant factors that control the heterogeneous ice nucleation process, the stochastic versus deterministic framework (Niedermeier et al., 2011; Vali, 2014). The stochastic framework assumes that freezing occurs randomly across a particle's surface and can be constrained with a temperature dependent nucleation rate (Pruppacher and Klett, 1997). This effectively yields time dependent freezing and an element of non-repeatability (Vali, 2008). On the other hand in the deterministic framework ice nucleation is dictated by ice active surface sites (Fletcher, 1969; Levine, 1950; Meyers et al., 1992; Sear, 2013). Each active site has a characteristic critical freezing temperature, with the site with the highest critical temperature always initiating crystallization instantly (Vali, 2008). Careful examination of the experimental results published by Vali (2008) indicates that the very nature of the process need not be in contention. These results suggest that there is a strong spatial preference on where nucleation occurs, supporting a model of discrete active sites. However, temperature fluctuations still occur indicating that a stochastic element also exists. Considering several decades of experimental work and theoretical considerations (Ervens and Feingold, 2013; Murray et al., 2012; Vali and Stransbury, 1966; Vali, 1994, 2014; Wright and Petters, 2013; Wright et al., 2013), the role of time has been determined to play a much weaker role than temperature does. It remains to be seen whether the difference is significant enough for time-dependent freezing to be completely omitted in atmospheric models.

The debate over how to properly parameterize heterogeneous ice nucleation has important implications on how freezing processes are represented in atmospheric models (Hoose and Möhler, 2012; Hoose et al., 2010; Koop et al., 2000; Phillips et al., 2008, 2012), and also reflects our fundamental understanding of this nucleation process. Ervens &

Deleted: (Hoose and Möhler, 2012; Hoose et al., 2010; Koop et al., 2000; Phillips et al., 2008, 2013), and also reflects our fundamental understanding of this nucleation process.

Feingold (2012) tested different nucleation schemes in an adiabatic parcel model and found that critical cloud features such as the initiation of the WBF process, liquid water content, and ice water content, all diverged for the different ice nucleation parameterizations. This strongly affected cloud evolution and lifetime. The divergence was even stronger when the aerosol size distribution was switched from monodisperse to polydisperse.

Deleted: properties

Deleted: further exaggerated as

Deleted: system gained complexity – for example by switching the

Deleted: ice nucleating particle size distributions

Deleted: a

Deleted: distribution. This indicates that with more sophisticated and realistic systems the variations between the modeled results caused by different freezing parameterizations can be even more drastic

A new parameterization, based on classical nucleation theory, is formulated in this paper. The new framework is stochastic by nature to properly reflect the randomness of ice embryo growth and dissolution, and assumes that an ice nucleating particle can exhibit variability in active sites along its surface, what will be referred to as internal variability, and variability in active sites between other particles of the same species, what will be referred to as external variability. A new method is presented to analyze and interpret experimental data from the ubiquitous droplet freezing cold plate method using this framework, and parameterize these experimental results for use in cloud parcel models. New insights into the proper design of cold plate experiments and the analysis of their immersion freezing datasets to accurately describe the behavior of atmospheric ice nucleating particles are revealed. Based on experimental observations and the new framework we argue that active site schemes that assume uniform active site density such as the popular n_s parameterization – a deterministic framework that assigns an active site density as a function of temperature (Hoose et al., 2008; Vali, 1971) – are unable to consistently describe freezing curves over a wide surface area range. This shortcoming is argued to be one of the causes of the discrepancies in retrieved n_s values of the same ice nucleating species using different measurement methods and particle in droplet concentrations (Emersic et al., 2015; Hiranuma et al., 2015a; Wex et al., 2015).

2 Classical nucleation theory

Ice nucleation is a fundamentally stochastic process brought about by the random formation, growth, and dissolution of critically sized ice germs that overcome the energy barrier associated with the phase transition (Pruppacher and Klett, 1997; Vali and Stransbury, 1966). A homogenous ice nucleation rate for a given volume of supercooled water can therefore be defined from a Boltzmann type formulation:

$$J(T) = C\exp\left(-\frac{\Delta G}{kT}\right) \qquad (1)$$

where J is the ice nucleation rate and has units of freezing events/(time × volume). ΔG is the energy barrier to crystallization from liquid water as defined in Pruppacher & Klett (1997) and Zobrist et al. (2007). T is temperature, k the Boltzmann constant, and C is a constant. For typical cloud droplet volumes, a temperature of about -38 °C is typically required for the homogeneous ice nucleation rate to become significantly fast such that freezing occurs within minutes or less. At temperatures between -38 and 0 °C a catalyst is required to initiate freezing of cloud droplets. Certain rare aerosol particles – ice nucleating particles – can act as these catalysts and induce heterogeneous ice nucleation in the atmosphere.

In expanding to heterogeneous ice nucleation the simplest approach is to assume that instead of ice germ formation occurring randomly throughout a bulk volume of supercooled water, ice nucleation is initiated on a surface. The surface reduces the nucleation energy barrier ΔG by a factor f, dependent on the contact angle between liquid water and the material. The contact angle θ $[0, \pi]$ is actually a proxy for the water-surface interaction system, with smaller values of θ indicating that the surface is a better nucleant. The surface's measured water contact angle cannot actually be simply used to predict its ice nucleation efficiency. The extreme limit of a contact angle of 0° is therefore a perfect ice nucleant, diminishing the energy barrier fully and immediately inducing freezing at the thermodynamic freezing point of water at 0 °C. The heterogeneous ice nucleation rate for a volume of water containing a total surface area of ice nucleating particles (INP) therefore can be defined as (Pruppacher and Klett, 1997):

$$J(T) = C\exp\left(-\frac{f(\theta)\Delta G}{kT}\right) \qquad (2)$$

where J in this case would be expressed as freezing events/(time × surface area).

The simplest stochastic formulation hypothesizes that the nucleation rate is uniform across the ice nucleating particle's surface, i.e. makes a single contact angle assumption. For a large statistical ensemble of droplet-INP pairings the number of frozen droplets after

Formatted: Font:Italic
Deleted: $Cexp$
Formatted: Font:Italic
Formatted: Font:Italic
Formatted: Centered, Tabs:Not at 5.5"
Formatted: Font:Italic
Deleted:

Formatted: Centered
Deleted: $Cexp\left(-\frac{f(\theta)\Delta G}{kT}\right)$
Deleted:

some time t resembles a first order chemical decay (Pruppacher and Klett, 1997; Vali, 2008):

$$N_f(T,t) = N(1 - \exp(-J(T)At)) \qquad (3)$$

Deleted: This pure stochastic formulation (also known as classical nucleation theory (Vali, 2008)) hypothesizes that the nucleation rate is uniform across the ice nucleating particle's surface. For a large statistical ensemble of droplet-INP pairings the number of frozen droplets after some time *t* resembles a first order chemical decay (Pruppacher and Klett, 1997; Vali, 2008):

Formatted: Centered

Deleted:

where N_f is the fraction of droplets frozen after time t at temperature T, N is the total number of particle-droplet pairings and A is the surface area of each individual ice nucleating particle (assumed to be the same for all particles). Furthermore, a probability of ice nucleation, P_f, at the single droplet-particle level can be defined as:

Deleted: .

$$P_f = 1 - \exp(-JAt) \qquad (4)$$

Formatted: Centered

Deleted:

3 Formulation of g: a continuum approach of active site activity to describe heterogeneous ice nucleation

Given the large variability in particle surface composition and structure across any one particle, which in turn determines the activity (or contact angle, θ) of a potential ice nucleating site, a different approach is to assume that the heterogonous nucleation rate will vary along the particle-droplet interface. Since the critical nucleation area (~nm^2) is much smaller than the total particle area (~µm^2), we apply a continuum assumption for the ice active site activity (θ) available across a particle's surface without assumptions about the size or number of active sites per particle surface area. The new resulting probability of freezing is:

Deleted: A more realistic approach is to recognize that the heterogonous nucleation rate will vary along the particle-droplet interface given

Deleted: each discrete ice active surface site.

$$P_f = 1 - \exp\left(-t \int J\, dA\right) \qquad (5)$$

Formatted: Centered, Indent: First line: 0"

Deleted:

where J is now a freezing rate that is allowed to vary for each specific small segment of the particle's surface area, dA. To define the freezing probability as a function of a contact angle distribution, the surface integral (Eq. 5) is transformed into a line integral via the newly defined g parameter and normalized to the total available surface area:

Deleted: infinitesimally

$$g(\theta) = \frac{1}{A}\frac{dA}{d\theta} \qquad (6)$$

and the freezing probability for a droplet-particle pair becomes:

$$P_f = 1 - \exp\left(-tA\int_0^{\pi} J(\theta)g(\theta)d\theta\right) \qquad (7)$$

g is a probability density function describing the continuous active site density of the ice nucleating particle's surface. This is the first use of a continuum description of active site density to our knowledge. Some key unique features of our approach are that the number or size of the individual active sites do not have to be assumed or retrieved in order to predict the freezing probabilities. The causes of these unique features in our framework and the choice of a normal distribution for the contact angle will be explored and justified in a following section.

In this work the *internal* variability of an individual ice nucleating particle expresses the heterogeneity of its ice nucleating surface. A wider (larger σ) g distribution describes a greater particle internal variability of ice active surface site properties or contact angles present on that one particle. This is in contrast to the *external* variability of an ice nucleating species, which expresses how diverse a population of particles is in their ice nucleation activities. External variability accounts for differences in the g distributions of individual particles between particles of the same type (such as particles composed of the same mineral phases).

Deleted: The

We hypothesize that experimentally probed systems can be interpreted as exhibiting internal and external variability based on differences in freezing temperatures of different droplets containing the same material, i.e. the freezing temperature spectrum of a droplet array. The model will be shown to provide a conceptual explanation of what this variability, be it internal or external, stems from. We provide this as a potential explanation for discrepancies in the measured values of the popular deterministic scheme n_s (Hoose and Möhler, 2012; Vali, 2014) for different particle concentrations and consequently different measurements methods. In the following sections the model is developed further to shed light on the impact of the g distribution on time dependent freezing, the contrasting internally and externally variable nature of a species' ice nucleating activity, and the dependence of g on particle size.

Deleted: Formulating a heterogeneous ice framework in this manner provides direct insight into the underlying causes of the freezing activity spectrum present in experimentally probed realistic particle systems that possess considerable internal and external variability. In the following sections the model is developed further to shed light on the impact of the g distribution on time dependent freezing, the contrasting internally and externally variable nature of a species' ice nucleating activity, and the complex dependence of g on particle size.

3.1 Internal variability and its impact on time dependent freezing

To explore the importance of accounting for ice nucleating variability along a single particle's surface (internal variability) we examined the temperature dependent freezing curves of droplets with single large ash particles immersed in them from Fornea et al. (2009). Their experiments were performed with cooling rates of 1 °C/min. Figure 1 displays their experimental data (red dots), a single contact angle (θ) fit to their data (red solid line) that assumes no internal variability, and a g distribution fit using multiple θs (solid blue line) that allows for internal variability. Fornea et al. retrieved their experimental data points by averaging the observed freezing temperature of the same ash particle-droplet pair after multiple freezing cycles. The averaged values are denoted freezing probabilities since they represent the chance of freezing occurring at that temperature. The ash particle diameter was around 300 μm, clearly much larger than atmospheric particle sizes.

To fit a g distribution to an empirical freezing curve, a least square error approach is implemented. A matrix of freezing probabilities is generated for all possible g distributions. If the experimental freezing curve has been retrieved from experiments in which the temperature is dictated by a non-constant cooling rate, an expression that satisfies this condition must be used:

$$P_f = 1 - \exp\left(-A \int_0^t \int_0^\pi J(T(t),\theta) g(\theta) d\theta dt\right) \qquad (8)$$

In equation (8) J is a function of time because temperature varies with time. If the cooling rate $\dot{T}$ is constant, a simple change of variable can be applied:

$$P_f = 1 - \exp\left(-\frac{A}{\dot{T}} \int_{T_i}^{T_f} \int_0^\pi J(T,\theta) g(\theta) d\theta dT\right) \qquad (9)$$

Equation (9) is therefore used to fit the constant cooling rate dataset from Fornea et al. (2009) considered here as well as datasets considered later in the paper.

Deleted: Fornea et al. (2009)

Deleted: $\exp\left(-A \int_0^t \int_0^\pi J(t,\theta) g(\theta) d\theta dt\right)$

Deleted: Fornea et al. (2009)

The g fit performs much better in capturing the behavior of the observed freezing temperature spectrum in Fig. 1, as expected given the greater degrees of freedom allowed for the multiple θ fit. The single θ fit has a steeper dependence on temperature; the double exponential temperature dependence of the freezing probability in Eq. (4) (J is an exponential function of temperature in itself as can be seen in Eq. (2)) results in an approximately temperature step function. The diversity of nucleating ability on the particle surface captured by the g parameter offsets some of the steepness and yields a more gradual freezing curve, more similar to the actual experimental freezing probability curve.

Deleted: Figure

Deleted: , a natural result of the formulation of classical nucleation theory from

Deleted: The non-step function nature of the measured freezing probabilities versus *T* also provides indirect evidence for internal variability in active site ability across one particle – otherwise the droplet-particle pair should freeze every time at the same *T*.

Two droplet freezing probability fits (dotted lines) are also plotted in Fig. 1 under different environmental conditions. Instead of prescribing a cooling rate the freezing probabilities are generated by running Eq. (7) for the entire temperature range with each fit for $\Delta t = 1$ hour. One fit uses the same g distribution used previously, while the additional single θ fit is approximated as a normal distribution with a near zero standard deviation, similar to a Delta Dirac function. The resultant freezing probabilities are then computed and plotted for every T. It can be seen that the g fit retains much stronger time dependence, with the freezing probability curve shifting about 5 K warmer and the single θ curve shifting just 1 K warmer for the 1 hour hold time.

Deleted: Figure

Deleted: at a constant

Deleted: of 255.5 K

Deleted: constant

Deleted: after

This numerical exercise shows that wider g distributions yield stronger time dependence due to the partial offset of the strong temperature dependence that the nucleation rate in Eq. (2) exhibits. The result emphasizes that how the active sites are modeled has consequences on what physical parameters (e.g. time, temperature, cooling rate) can influence the freezing outcome and observed droplet freezing temperature spectrum (Broadley et al., 2012). In Fig. 1 a wider g distribution resulted in higher sensitivity to time, which resulted in a shift of the freezing curve to higher temperatures as the system was allowed to temporally evolve at a fixed temperature. This significant change in the freezing probability's sensitivity to temperature is the cause of the more gradual rise in the freezing probability for the system when applying a non-Delta Dirac g distribution. This is effectively enhancing the stochastic element in the particle's ice nucleation properties. The shallower response of freezing probability to decreasing temperature (deterministic freezing) creates a greater opportunity for time-dependent (stochastic freezing) to manifest, as a larger fraction of the droplets spend more time unfrozen. The enhancement of the stochastic element brings about a more important role for time as shown in Fig. 1. The finding of this exercise is consistent with previously published work on time dependent freezing such as those reported by Barahona (2012), Vali and Stransbury (1966), Vali, (1994b), and Wright and Petters (2013), amongst others.

3.2 Defining *g* as a normal distribution of ice nucleation activity

The fit for a particle-freezing curve such as the one considered in the previous section (Fig. 1) does not have a unique solution. There are, mathematically speaking, infinite solutions for the *g* distributions that produce a representative freezing curve. In any considered distribution an ascending tail with increasing contact angle represents a competition between more active but less frequent surface sites, and less active but more frequent sites. Sites with lower activity and lower frequency have essentially zero chance of contributing to the overall freezing probability, primarily due to the nucleation rate's, *J* exponential dependence on the energy barrier to nucleation and the freezing probability's exponential dependence on *J* as shown in Eqs. (2) and (7). It is therefore sufficient to conceptualize that the particle has a well-defined monotonic spectrum of active sites increasing in frequency while decreasing in strength. The spectrum is modeled as a continuum of ice nucleation activity described by the *g* distribution, as depicted on the upper right hand corner in Fig. 2. Figure 2 also shows part of the *g* distribution (the ascending part representing the monotonic spectrum of active sites) retrieved for the case example in section 3.1 (log scale) discretized into numerical bins, where the height of each bin represents the abundance of that θ across the particle's surface. The area in each column thus represents the total surface area with that value of θ. As in Fig. 2's inset the darker colors are used to emphasize more active ice nucleating activity at the smaller contact angles.

The ascending part of the curve of the normal *g* distribution covering the smallest (most active) values of θ in Fig. 2 can therefore capture this active site model. The wider the defined *g* distribution (i.e. for a larger standard deviation, σ) the more diverse the

Deleted: Wider *g* distributions therefore yield stronger time dependence due to the partial offset of the strong temperature dependence that classical nucleation theory exhibits. The result emphasizes the importance of accounting for internal variability, as it has consequences on what physical parameters (e.g. time, temperature, cooling rate) can influence the freezing outcome and observed droplet freezing temperature spectrum (Broadley et al., 2012). In Fig. 1 a wider *g* distribution resulted in higher sensitivity to time, which resulted in a shift of the freezing curve to higher temperatures as the system was allowed to temporally evolve at a fixed temperature. ... [2]

Deleted: **active site**

Deleted: ascent in the curve

Deleted: rate *J*'s

Deleted: one large effective active site relevant to the ice nucleation process that actually manifests – that causes the particle-droplet system to freeze. This site has

Deleted: ... [3]

Deleted: curve of the normal

Deleted: covering

Deleted: smallest (most active) values of θ in Figure 2 can capture this active site model.

Moved down [1]: The wider the defined *g* distribution (i.e. for a larger standard deviation, σ) the more diverse the considered system is in its internal variability of ice nucleation activity.

Deleted: Simply put the single contact angle description (e.g. red fit line in Fig. 1) is in a way applicable, as long as slight variation around that value of θ is considered to account for the surface diversity

Deleted: . The variation would encompass the minimum amount of internal variability needed to properly model the freezing behavior of the droplet containing the ice nucleating particle. Since the freezing probability is determined solely by a fraction of the ascent of the normal distribution – as this captures the rare but most active sites that determine the actual freezing rate *J* and freezing probability P_f – the following approximation to equation (7

Moved down [2]:) can be made: ... [4]

Moved down [3]: (10) ... [5]

Formatted: Font:Italic

Deleted: $\left(-tA\int_0^{\pi} J(\theta)g(\theta)d\theta\right) \approx 1 - \exp\left(-tA\int_{\theta_{c_1}}^{\theta_{c_2}} J(\theta)g(\theta)d\theta\right)$

Deleted: ... [6]

Deleted: The curve in Fig. 2 only displays part of the ascent of the *g* distribution and in particular the critical contact angle range for small θ values, $[\theta_{c_1}, \theta_{c_2}]$.

Moved (insertion) [1]

considered system is in its internal variability of ice nucleation activity. Since the freezing probability is determined solely by a fraction of the ascent of the normal distribution – as this captures the rare but most active sites that determine the actual freezing rate J and freezing probability P_f – the following approximation to Eq. (9) can be made:

$$P_f = 1 - \exp\left(-\frac{A}{\dot{T}}\int_{T_i}^{T_f}\int_{0}^{\pi} J(T,\theta)g(\theta)d\theta dT\right)$$

$$\approx 1 - \exp\left(-\frac{A}{\dot{T}}\int_{T_i}^{T_f}\int_{\theta_{c_1}}^{\theta_{c2}} J(T,\theta)g(\theta)d\theta dT\right) \qquad (10)$$

where θ_{c_1} and θ_{c_2} are the approximate cutoff points in the g distribution that contain the critical range of the most active contact angles. Outside $[\theta_{c_1}, \theta_{c_2}]$ the less active contact angles have a negligible contribution to the actual manifested freezing rate and freezing probability. The critical contact angle range is a strong function of the area of the particle.

The critical contact angles are determined numerically by identifying the range $[\theta_{c_1}, \theta_{c_2}]$ for which the freezing probability can be approximated using Eq. (10). Figure 3(a) illustrates the process of identifying θ_{c2}. The blue curves represent freezing probabilities computed via integrating Eq. (10) from 0 to a variable θ_{c2}. The red curve is the freezing probability computed from integrating across the full θ range. As θ_{c2} is increased the resultant curve (blue) approaches the curve computed from the full θ range (red). For the example studied in Fig. 3 (same system examined in Section 3.1), a value of $\theta_{c2} = 0.79$ rad captures 99.9% of the complete freezing probability found using the full range of θ.

Furthermore, the critical contact angle range can be used to estimate a hypothetical nucleating area of the particle – the total active site surface area where nucleation will take place. The nucleation area $A_{nucleation}$ can be estimated as follows:

$$A_{nucleation} = A\int_{\theta_{c_1}}^{\theta_{c_2}} g(\theta)d\theta \qquad (11)$$

For the large ash particle system analyzed in the previous section (Fig. 1) it is estimated that for its estimated diameter of 300 μm and a cooling rate of 10 K/min $\theta_{c1} \approx 0.4$ rad and

Moved (insertion) [2]

Formatted: Font:Italic

Moved (insertion) [3]

Deleted: that satisfies

Deleted: system

Deleted: ,

Deleted: 1.1

Deleted: provides quantitative insight into the

Deleted:

$\theta_{c2} \approx 0.79$ rad. Application of Eq. (11) yields a total ice active surface area estimate of 27 nm^2. Classical nucleation theory estimates that the area of a single active site is 6 nm^2 (Lüönd et al., 2010; Marcolli et al., 2007). The estimated total area of nucleation is therefore consistent with this value and supports the argument that competition between sites along the critical range of θ is taking place. However, the surface area where ice nucleation is occurring remains a very tiny fraction of the total particle surface. This further justifies the use of a continuum of surface area to define g as $dA/d\theta$ (Eq. 6). The nucleating area is a function of both the g Gaussian distribution of θ, and the total surface area of the considered particle. Figure 3(b) shows the g distribution in log scale and highlights in red the fraction of the distribution covered by the critical contact angle range.

3.3 Using critical area analysis to predict droplet freezing spectra obtained in cold plate experiments

Many droplet freezing array experimental methods such as those described in Broadley et al. (2012), Murray et al. (2011), Vali (2014), Wright & Petters (2013), and Hiranuma et al. (Hiranuma et al., 2015a) use atmospherically relevant particle sizes (hundreds of nanometers to a few microns in diameter) but create the droplet array from a prepared suspension of the particles of interest in water. The resultant particle concentrations are typically high and the number of particles present in each droplet has to be approximated using statistical methods. When total particle surface area is high enough we hypothesize that it is conceivable that a threshold is reached whereby most of the species' maximum possible external variability is already available within the particle-droplet system. At this point it is approximated that no additional diversity in external variability (ice active site ability or θ) is created by further increasing the total particle surface area in the water volume; the external variability has effectively saturated. For the application of this model to cold plate data where droplets are prepared from a suspension of the species being investigated, the particle population in each droplet is treated as one aggregate surface and a mean surface area value is assumed for particle material in all the droplets in the array. This estimate is retrieved from the weight percentage of the material in the water suspension and our best guess for a reliable surface area density.

Past the hypothesized surface area threshold, which will be referred to as the critical area, each member of the system's population (droplets with particles immersed in them) become approximately identical in their ice nucleation properties and the theoretical frozen fraction can be expressed as:

$$F = P_f(one\ \text{system}) = 1 - \prod_{i=1}^{n} P_{uf,i} \qquad (12)$$

where F is the droplet frozen fraction, n is the number of particles per droplet, and $P_{uf,i}$ is the probability that the particle i does not freeze. Further expanding the expression yields:

Deleted: system

$$F = 1 - \exp\left[-t\left(\sum_{i=1}^{n} A_i \int_0^{\pi} J(\theta) g_i(\theta) d\theta\right)\right] = 1 - \exp\left[-t \int_0^{\pi} J(\theta) \sum_{i=1}^{n} (A_i g_i) d\theta\right] \quad (13)$$

Next the parameter $\bar{g}$ is defined:

$$\bar{g} = \frac{\sum_{i=1}^{n}(A_i g_i)}{A_t} \qquad (14)$$

where A_t is the sum of all particle surface area available inside a given droplet, and A_i is the surface area representing that value of g_i (which is a function of θ). Equation (13) then becomes:

$$\Rightarrow F = 1 - \exp\left(-tA_t \int_0^{\pi} J(\theta)\overline{g(\theta)} d\theta\right) \qquad (15)$$

Formatted: Centered

Deleted:

$\bar{g}$ is the arithmetic average of all the g distributions for ensemble of particles in the droplet (each particle has its own g distribution) with a cumulative area larger than the critical area of the species they belong to. Alternatively $\bar{g}$ can be thought of as the probability density function for all possible ice nucleating activity of a given species or particle type. It is worth mentioning that $\bar{g}$ is a true continuous probability density function. While the g distribution of an individual particle is an approximate continuous function – due to the very small size of ice nucleating active sites – $\bar{g}$ contains all possible values of contact angles that an ice nucleating species can exhibit.

Deleted: a statistically significant

Deleted:).

Above a certain surface area threshold it is conceptualized that the chance of an ice-nucleating particle surface not possessing the entire range of ice nucleating activity (θ)

Deleted: probability

becomes very small. The model therefore assumes that any particle or ensemble of particles having a total surface area larger than the critical area can be approximated as having $\bar{g}$ describe the actual g distribution of the individual particles. In other words, for large particles with more surface area than the critical area threshold, it is assumed that the external variability between individual particles will be very small such that the particle population can just be described by one average continuous distribution of the ice active site ability, $\bar{g}$.

To resolve the active site distributions of the systems possessing particle surface areas smaller than the critical area the first step is to approximate the critical area. Experiments must start at very high particle surface area concentrations to ensure the number of particles and total surface area per droplet exceeds the critical area. For the illite mineral particle case study considered next, for example, high particle concentrations were those that resulted in total particle surface areas greater than about 2×10^{-6} cm^2. The particle number or surface area concentration is then decreased until the retrieved g distribution (from the measured droplet freezing temperature spectrum for an array of droplets containing particles) can no longer be reasonably predicted by $\bar{g}$. This point can identify the parameter A_c, the critical area of the species under study. A schematic of the procedure is summarized in Fig. 4.

Figure 5 shows experimental freezing curves (open symbols) taken from Broadley et al. (2012), with different particle surface area concentrations. 10-20 µm droplets were used and cooled at a cooling rate of 5 K/min. The curves from the highest particle concentration experiments, $7.42\text{x}10^{-6}$ cm^2 (6b) and $2.02\text{x}10^{-6}$ cm^2 (6a), are used to approximate the critical area of the system by first fitting the 6b curve with a g distribution and then successfully predicting the 6a curve with the same g distribution obtained from 6b and applying a particle surface area correction. The fit to the 6b curve is done using Eq. (9) and follows the same procedure of least square error fitting described in section 3.1. This g distribution is therefore assumed to be the $\bar{g}$ of the considered system with $\mu = 1.72$, and $\sigma = 0.122$. Note that above the threshold concentration A_c, approximated here as occurring around $7.42\text{x}10^{-6}$ cm^2, a change in the total available surface area A is all that is required to account

Deleted: This threshold surface area will be referred to as the critical area. Any

Deleted: reliably

Deleted: .

Deleted: g

Deleted: determine this threshold of statistical significance.

Deleted: statistical significance.

Deleted: .02

Deleted: averaged

Deleted: significantly diverges from

Deleted: Figure 4 also plots the popular exclusively deterministic scheme's ice active site density parameter n_s (Vali, (2008), Murray et al. (2011), Broadley et al. (2012), Hiranuma et al. (2015), and Wex et al. (2015), amongst others), retrieved directly from freezing curves of droplets with illite particles immersed in them measured in a cold plate system by Broadley et al. (2012)

Moved down [4]: and used to produce the right panel in Fig. 4.

Deleted: Similar to $\bar{g}$, n_s assumes active site diversity can be defined independently of the surface area (it is multiplied by total surface area to estimate total heterogeneous ice nucleation activity).

Moved down [5]: As the total particle surface area of the system under study is reduced from the blue to the red curve, the retrieved n_s values are similar indicating that variability of active sites remains constrained within droplets. Note that both the red and blue curves were obtained from systems we have determined were above the critical area threshold

Deleted: .

Moved down [6]: Further reduction of total surface area to below the critical area threshold shifts the n_s values ... [7]

Deleted: The curves plotted in Fig. 4 were derived u ... [8]

Moved down [7]: We have observed other similar ... [9]

Deleted: This includes droplet freezing measurem ... [10]

Moved down [8]: A contact angle θ_r

Deleted: is randomly selected and the value of the ... [11]

Moved down [9]: n_{draws} is the only parameter th ... [12]

Deleted: The sampled g distributions are normaliz ... [13]

Moved down [10]: distributions the freezing pr ... [14]

Deleted: ... [15]

Moved down [11]: At higher surface areas they ... [16]

Deleted: For larger droplets the transition seemed ... [17]

Deleted: all

Formatted: Not Superscript/ Subscript

Deleted: confirm statistical significance

Deleted: , since external variability has saturated.

for how the change in particle concentration shifts the droplet freezing temperature curve. This is not the case when total area is less than the critical area A_c, as discussed next.

Moving to the lower concentration freezing curves (1.04×10^{-6} cm^2 – 5a; and 7.11×10^{-7} cm^2 – 4a) the transition to below the critical area begins to be observed. The solid lines attempt to predict the experimental data points using $\bar{g}$. Predicting experimental data points for the 1.04×10^{-6} cm^2 (5a) system with the same $\bar{g}$ distribution captures the 50% frozen fraction point but fails at accounting for the broadness on the two ends of the temperature spectrum. The prediction from $\bar{g}$ completely deteriorates in quality for the lowest concentration experiments (7.11×10^{-7} cm^2 – 4a) as it neither captures the temperature range over which freezing is occurring nor the 50% frozen fraction point.

We investigated a similar trend when freezing droplets containing commerical Snomax (York International), and MCC cellulose (Sigma-Aldrich) particles immersed in oil in our in-house cold plate system, described by Polen et al. (2016). The relevant system details are that particle containing water droplets of approximately 450-550 µm in diameter are immersed in squalane oil, analogous to the method of Wright et al. (2013), and the droplets' freezing temperature is determined optically during a constant 1 K/min cooling cycle. Figure 6 shows decreasing concentration freezing curves for droplets containing Snomax particles. Snomax is a freeze-dried powder manufactured from non-viable *Pseudomonas syringae* bacteria and is commonly used to make artificial snow due to its very mild freezing temperature of -3 to -7 °C. Its ice nucleation properties are attributed to large protein aggregates, and Snomax is often used as a proxy for atmospheric biological INP (Wex et al., 2015). A similar approach was undertaken in which $\bar{g}$ was retrieved using the highest concentration freezing curve (solid blue line). The surface area density is assumed to be 1 m^2/g though it is recognized that given the protein aggregate based ice nucleating mechanism of Snomax it is difficult to attribute a surface area of nucleation to a mass of Snomax powder. However, a surface area value needs to be assumed to retrieve the ice nucleating properties using the framework presented here for the sake of comparing Snomax to the other systems. For an assumed critical area of 4×10^{-6} cm^2 (the surface area at 0.1 wt%) $\bar{g}$ was found to have $\mu = 0.66$, and $\sigma = 0.055$. Unlike the illite dataset considered first, only 50% of the freezing behavior of the second highest concentration

Deleted:

Deleted: , and what follows is a method to predict these low particle concentration-freezing curves

Deleted: statistically significant

Deleted: take place

Deleted: statistically significant

Deleted: measurements

Deleted: statistically significant

Deleted: ($\bar{g}$)

Deleted: shape

Deleted: If however the

freezing curve is captured by a frozen fraction retrieved from $\bar{g}$ (solid red line). Further lowering the concentration produces a similar trend previously observed for the droplets containing illite, with similar freezing onsets at higher temperatures but significant divergence at lower temperatures (purple and green points). The frozen fractions retrieved from $\bar{g}$ for the 0.08 wt% and 0.07 wt% Snomax droplets (not plotted, as they almost overlap with the solid red line) do not capture any of the freezing behavior measured indicating a very sensitive dependence of active site density on surface area. A notable difference from the droplets containing illite is that there is significant weakening in ice nucleation ability as the concentration/surface area of Snomax is reduced. A potential explanation for this effect in the context of the framework presented here will be discussed in a following section.

The freezing curves from droplets containing MCC cellulose powder (Hiranuma et al., 2015b) are shown in Fig. 7. For the MCC cellulose freezing curves $\bar{g}$ was found to have $\mu = 1.63$, and $\sigma = 0.12$, from the 0.1 wt% curve. The freezing curve retrieved from droplets containing 0.1 wt% (blue) cellulose was estimated to be the critical area transition value as the second highest concentration freezing curve (0.05 wt%, red) can be predicted directly from $\bar{g}$. Assuming a surface area density of 1.44 g/m^2 (Hiranuma et al., 2015a) the critical area for MCC cellulose is estimated to be ~9.4×10^{-4} cm^2. MCC cellulose appears to exhibit ice nucleating capabilities reasonably stronger than illite and significantly weaker than Snomax, based on the observed freezing temperature spectra and the $\bar{g}$ values retrieved. $\bar{g}$ for Snomax was 0.66 ± 0.055, 1.72 ± 0.122 for illite NX, as compared to 1.63 ± 0.12 for MCC cellulose.

To predict the freezing curves of the droplets with particle surface areas lower than the estimated critical area for the systems considered here, the aggregate surface area of the entire particle population within each droplet is modeled as one large surface. A contact angle θ_r is randomly selected from the full contact angle range [0, π], and the value of the active site distribution g^* for the particle i being sampled for at θ_r is assigned the value of $\overline{g(\theta_r)}$:

$$\left(g_i^*(\theta_{r,n_{draw}})\right) = \overline{g(\theta_r)} \qquad (16)$$

Moved (insertion) [8]

The g^* distributions within this numerical model are given an asterisk to indicate that they are discrete distributions.

This process is repeated for a parameter n_{draws}, for each droplet in the array that produced the freezing curve being modeled. n_{draws} is the only parameter that is optimized for so the modeled freezing curves can predict the behavior of the experimental freezing curves. The value of n_{draws} typically ranges from 9 to 65 for the systems analyzed here and is therefore a relatively soft optimization parameter with small dynamic range. The sampled g^* distributions are normalized with respect to the estimated total surface area for the freezing curve being modeled before being used to compute the freezing probability. The bottom part of Fig. 4 shows a schematic of how g^* is retrieved from $\bar{g}$ using n_{draws}. With the sampled g^* distributions the freezing probability of each droplet is calculated using Eq. (9) and the frozen fraction curve is computed from the arithmetic average of the freezing probabilities:

$$F(below\ critical\ area) = \frac{1}{N}\sum_{i=1}^{N} P_{f_i} \qquad (17)$$

where N is the number of droplets in the cold plate array.

The behavior of the experimental curve is captured using the n_{draws} numerical model in which random sampling from the ice nucleating spectrum dictated by $\bar{g}$ is carried out to predict the freezing curve. The dotted lines in Figs. 5, 6, and 7 are obtained by sampling from the $\bar{g}$ model to successfully predict the behavior of all the freezing curves. The early freezing onsets of the lower concentration systems as well as the broadness in the curves are both captured with the model. After $\bar{g}$ was obtained from the high concentration data above the critical area threshold, the only parameter that had to be optimized to produce these accurately predicted freezing curves was n_{draws}. The values of n_{draws} for the lower concentration freezing curves for each of the systems investigated here are 21 (2.02x10^{-6} cm^2), 19 (1.04×10^{-6} cm^2), and 11 (7.11×10^{-7} cm^2) for the droplets containing illite; 65 (0.09 wt%), 48 (0.08 wt%), and 23 (0.07 wt%) for the droplets containing Snomax; and 21 (0.05 wt%), 11 (0.01 wt%), and 9 (0.001 wt%) for the droplets containing cellulose. It should also be noted that there is an n_{draws} value for each system above for which the sampled

Moved (insertion) [9]

Deleted: is used,

Moved (insertion) [10]

Deleted: a

Deleted: , the behavior of the experimental curve is both qualitatively and quantitatively captured.

Deleted: are captured with the model distribution mimics $\bar{g}$. For example, when n_{draws} is 25 for the illite system the retrieved distribution will produce a freezing curve equivalent to using $\bar{g}$

Perhaps the most notable characteristic is how the freezing curves of all three systems analyzed ascend together early as temperature is decreased but then diverge as the temperature decreases further (Figs. 5, 6a, and 7a). The closeness of the data at warmer temperatures (the ascent) is interpreted by the framework as the presence of some rare high activity active sites within the particle population under all the particle concentrations explored in these experiments. At lower temperatures it appears that there is a wider diversity in the activity of droplets that did not contain these rare efficient active sites, and thus there is significant spread in the freezing curve for T < 242 K. In the context of the framework presented here this can be attributable to strong external variability of the ice nucleating population, with very strong/active nucleators causing similar freezing onsets for different particle concentrations at the warmer temperatures, and a lack of strong nucleators explaining the less consistent freezing of the unfrozen droplets at lower temperature. Thus it follows that there is a wider spread in the freezing curves for these droplets, as their freezing temperature is highly sensitive to the presence of moderately strong active sites. This expresses a greater diversity in external variability – the active site density possessed by individual particles from the same particle source. In a later section the claim of more external variability contributing to the broader curves below the critical area threshold is supported with a closer look at the numerical results from the model.

The droplets containing Snomax displayed an immediate shift in freezing behavior for small changes in concentration (from 0.1 wt% to 0.09 wt%) whereby a small drop in concentration and thus surface area resulted in a broader temperature range over which freezing of the droplets occurred (Fig. 6a). In the context of the model presented here this is due to the mode of the $\bar{g}$ distribution occurring at a very small (and thus very active) contact angle of 0.66. In this contact angle range the barrier to nucleation is greatly reduced causing freezing to be even more sensitive to the strongest active sites, and less sensitive to the competing active sites that are weaker but more abundant (depicted in Fig. 2), and therefore causing freezing curves to be quite steep versus T. A small change in the surface area of this material may have produced a significant reduction in the probability of

Deleted: accurate predicted freezing curves was n_{draws}. This optimization of n_{draws} can be omitted if a computationally expensive brute force calculation is applied where each particle surface is partitioned into small 1 nm^2 unit areas and random θ assignments are carried out for each.

Deleted: One

Deleted: these

Deleted: with decreasing

Deleted: .

Deleted: their experiments. As the single most efficient active site causes the entire droplet to freeze, so long as there is one such site in each droplet the same freezing temperature will be observed.

Deleted: This is probably due

Deleted: The droplets that freeze at lower temperatures are the “leftover” droplets that did not contain at least one very active surface site. Thus it makes sense

Deleted: activity

Deleted: statistically significant

droplets possessing these very strong nucleators, resulting in the observed broadening of the freezing curves. This trend in Snomax is further investigated in a following section.

Figure 4 also plots the popular exclusively deterministic scheme's ice active site density parameter n_s (Hiranuma et al., 2015a; Murray et al., 2012; Vali, 1971, 2008; Wex et al., 2015). n_s is an active site density function defined in the following equation:

$$F = 1 - \exp(-n_s(T)A) \qquad (18)$$

Moved (insertion) [12]

Deleted: ... [18]

Equation (18) is similar in mathematical form to Eq. (15) and inherently assumes that active site density can be defined as uniform over a particle's surface and is therefore independent of the total surface area (it is multiplied by total surface area to estimate total heterogeneous ice nucleation activity). From this point onwards n_s is regarded as the deterministic analog of $\bar{g}$, where any time-dependent (stochastic) freezing is omitted. The justification presented for the definition and use of the critical area quantity also applies to the n_s framework, where it is argued that n_s ceases to become a proper representation of the ice nucleation activity below the critical area threshold.

The values of n_s were retrieved directly from freezing curves of droplets with illite particles immersed in them measured in a cold plate system by Broadley et al. (2012) and used to produce the right panel in Fig. 4. As the total particle surface area of the system under study is reduced from the blue to the red curve, the retrieved n_s values are similar indicating that variability of active sites remains constrained within droplets. Note that both the red and blue curves were obtained from systems we have determined were above the critical area threshold (Fig. 4). Further reduction of total surface area to below the critical area threshold shifts the n_s values noticeably, as seen by the significant increase in n_s(T) for the green curve. As all three curves were obtained by just varying the particle concentration of the same species the same n_s values should be retrieved for all three curves; the n_s scheme is designed to normalize for the total surface area or particle mass present. This is successful for the higher particle surface area systems (red and blue curves are similar) but not at lower particle area (green curve diverges). The large increase in n_s observed when total surface area is below the critical area threshold indicates that the observed droplet freezing temperature spectra do not just linearly scale with particle concentration or surface area. Further analysis will show this is not due to an enhancement

Moved (insertion) [4]

Moved (insertion) [5]

Moved (insertion) [6]

of ice nucleating activity per surface area but is actually a product of external variability causing a broadening of the ice nucleating spectrum within the droplet ensemble when total surface area is below the critical area threshold.

We have observed other similarly large effects of particle concentration on the measured droplet freezing temperature spectrum and the retrieved n_s curves from our own cold plate measurements. Figures 6b and 7b display n_m (active site density per unit mass (Wex et al., 2015)) and n_s curves versus temperature for freezing droplets containing Snomax and MCC cellulose, respectively. Similar to the data in Fig. 4b, these two systems also exhibit a divergance in n_s (or n_m) as concentration (or surface area) is decreased. Droplets containing MCC cellulose exhibited a much stronger sensitivity to decreasing surface area than the droplets containing illite did, with changes in the values of n_s of up to four orders of magnitude. The droplets containing Snomax on the other hand were less sensitive to changes in surface area and exhibited an opposite trend in n_m, with the values of n_m *decreasing* with decreasing concnentration. This is consistent with the analysis of the Snomax freezing curves, where the ice nucleating activity experienced a substantial drop with decreasing surface area. It is further argued in a later section that this is due to the very sharp active site density function g that Snomax particles appaear to possess, resulting in steep droplet freezing temperature curves.

Moved (insertion) [7]

In assessing the three systems investigated here, it appears that the critical area threshold depends a lot on the strength ($\overline{g(\theta)}$) of the ice nucleating activity for that system. Capturing the critical area transition for illite required probing droplets that were an order of magnitude smaller than the droplets containing Snomax and cellulose, indicating a very large difference in the scale of the critical area. One explanation for this behavior is that when ice nucleating activity is weak, nucleation can occur over a larger total nucleating surface area. This means there is a smaller chance of losing critical active sites in a droplet as the amount of material is reduced with decreasing particle concentration. This argument is supported by these three data sets that span almost the entire heterogeneous ice nucleation temperature range.

For the illite mineral suspensions Broadley et al. (2012) identified two total surface area regimes by analyzing their droplet freezing curves. In the lower surface area regime they observed a different freezing dependence on particle surface area than at higher surface areas. At higher surface areas they saw no dependence of the freezing curves on total particle surface area, which is inconsistent with both the stochastic and deterministic frameworks. For larger droplets the transition seemed to occur at higher total particle surface area indicating that there might be a particle concentration effect impacting the total particle surface area per droplet. We have conducted our own illite measurements to investigate this high concentration regime and further probe the applicability of $\bar{g}$ to freezing curves above the identified critical area threshold. Figure 8 shows the frozen fractions versus temperature for an ensemble of droplets containing illite NX on our cold plate system. The concentrations used were 0.5 wt%, 0.3 wt, 0.25 wt%, 0.2 wt%, 0.1 wt%, 0.05 wt%, 0.03 wt%, 0.01 wt%, and 0.001 wt% and the droplets were cooled at a rate of 1 K/min. Average surface area estimates are made by assuming 500 μm diameter droplets and a surface area density of 104 m^2/g (Broadley et al., 2012). The solid lines are applications of Eq. (15) with the same $\bar{g}$ as the one found for the illite data set considered above. It can be seen that this $\bar{g}$ retrieved from cold plate experiments where droplets are on the order of 10-20 μm produces reasonable predictions of the freezing curves where droplets are on the order of 500 μm and thus contain particle surface areas up to five orders of magnitudes larger. Another important conclusion that can be drawn from this dataset is that high concentration data (0.25 wt%, 0.3 wt%, and 0.5 wt%) exhibited a similar plateauing in freezing temperatures despite additional amounts of illite. This is similar to the concentration range where Broadley et al. (2012) found a saturation effect when further increasing the concentration of illite (over 0.15 wt%). This supports the hypothesis that the high surface area regime for illite experiments is actually experiencing a particle mass concentration effect and not a total surface area effect. The fact that the concentration where this saturation effect is so similar while the droplet volumes and consequently the amount of illite present between the two systems is quite different points to a physical explanation such as particle settling or coagulation due to the very high occupancy of illite in the water volume. These physical processes could reduce the available particle surface area in the droplet for ice nucleation. Additionally, the high concentration freezing curves show a good degree of broadening in the temperature range over which freezing occurs. These three curves share a close 50% frozen fraction temperature (with the 0.5 wt% oddly

Moved (insertion) [11]

Deleted: The popular exclusively deterministic scheme (Broadley et al., 2012; Murray et al., 2012; Vali, 1994, 2008; amongst others) prescribes an ice active site density function n_s that is an intensive property of the species under study. The frozen fraction of the ensemble is computed from a time independent equation:

Moved up [12]: $F = 1 - \exp(-n_s(T)A)$ (18)

exhibiting a slightly lower 50% frozen fraction temperature than the other two). One explanation that is consistent with the hypothesis of particle settling and coagulation is that it becomes less likely that the droplets contain similar amounts of suspended material when they are generated from such a concentrated suspension (Emersic et al., 2015). This results in larger discrepancies in available surface area between the droplets and therefore a broader temperature range over which the droplets are observed to freeze.

3.4 Comparison between $\bar{g}$, n_s, and other existing parameterizations of heterogeneous ice nucleation

To our knowledge, this is the first heterogeneous ice nucleation parameterization that aims to attribute a surface area dependence to active site distributions of ice nucleating particles. The popular exclusively deterministic scheme (Broadley et al., 2012; Murray et al., 2012; Vali, 1994, 2008; amongst others) prescribes an ice active site density function n_s that is an intensive property of the species under study. Equation (15), derived from classical nucleation theory and used in the $\bar{g}$ model, and the deterministic-based Eq. (18) used in the n_s model, have a very close mathematical form. Both carry a negative exponential dependence on surface area, and the temperature dependence in the rest of the variables is inside the exponential.

Fitting freezing curves with droplets below the critical area threshold with n_s yields errors similar to fitting the curves with $\bar{g}$. Doing so has an inherent assumption of the ice nucleation activity being totally internally variable. This is clear in comparing Eqs. (15) and (18). That is $\bar{g}$ and n_s both offer incomplete information about the distribution of ice nucleation activity for a species. A similar conclusion along these lines was reached by Broadley et al. (2012) when the authors noted that the best fits to their freezing curves were achieved when the system was assumed to be totally externally variable. That is when each particle was assumed to have a single contact angle but a distribution assigned a spectrum of contact angles for each particle in the population.

There are other formulations that hypothesize an active site based or multi-component stochastic model such as the ones described in Vali & Stransbury (1966), Niedermeier et al. (2011), Wheeler and Bertram (2012), and Wright and Petters (2013). Vali and Stransbury (1966) were the first to recognize that ice nucleating surfaces are diverse and stochastic and thus active sites need to be assigned both a characteristic freezing temperature as well as fluctuations around that temperature. Niedermerier et al. (2011) proposed the soccer ball model, in which a surface is partitioned into discrete active sites with each site conforming to classical nucleating theory. Marcolli et al. (2007) found a Gaussian distribution of contact angles could best describe their heterogeneous ice nucleation data in a completely deterministic framework. Welti et al. (2012) introduced the alpha-PDF model where a probability density function prescribes the distribution of contact angles that a particle population possesses, such that each particle is characterized by a single contact angle. Wright and Petters (2013) hypothesized the existence of a Gaussian probability density function for a specific species, which in essence is similar to the $\bar{g}$ framework described here. The notable difference is that their probability density function was retrieved via optimizing for all freezing curves, and not from independently fitting high concentration freezing curves as we have done here.

The n_s scheme is now more commonly used to describe and compare cold plate and other experimental ice nucleation data instead of the multi-component stochastic schemes (Hiranuma et al., 2015a; Hoose and Möhler, 2012; Murray et al., 2012; Wex et al., 2015). This is in part due to the necessary inclusion of more variables required by other frameworks (such as prescribing a discrete number of active sites in the soccer ball model by Niedermeier et al. (2011)) than the simpler purely deterministic scheme of n_s. The new formulation described here requires only prescribing a species' heterogeneous ice nucleation ability as a function $\bar{g}$ along with finding the critical area, A_c. The critical area is determined by repeatedly measuring freezing curves for the same system or sample using different particle concentrations. Varying particle concentration is already routinely used in cold plate experiments to widen the droplet freezing temperature range that can be measured. An estimate of the total surface area of the particles under study must be made and associated with the retrieved freezing curves. While a process of random sampling using n_{draws} is initially necessary to predict the freezing curves at more atmospherically realistic concentrations below the critical area, in a following section we will introduce

Deleted: Niedermeier et al. (2011)

Deleted: Wright and Petters (2013)

Deleted:

Deleted: Stranbury

Deleted: However no distinction between curves below and above a critical threshold of total surface area was made as active site distributions sampled from the general distribution were generated to fit

Deleted: freezing curves. This required

Deleted: the hypothesized Gaussian distribution using

Deleted: . Their method also required making assumptions about the size of the active site, a parameter that does not necessarily need to be defined if the critical range of θ is carefully investigated

Deleted:

easy to apply parameterizations that derive from this sub-sampling of droplet freezing temperature spectra obtain above the critical area threshold.

3.5 Dependence of g on ice nucleating particle size

The particle size dependence of the freezing probability comes from the exponential dependence of the freezing probability on the surface area A as shown in Eq. (7). The freezing probability's sensitivity to surface area is the same as its sensitivity to time however the quadratic dependence of area on radius makes size a more sensitive parameter than time. Furthermore, there might be more subtle size dependencies in the g function itself. For a given particle type, whether size affects the diversity (internal variability) of nucleating sites is not something that can be trivially probed experimentally. To accurately test any potential size dependence, particles of varying sizes need to be probed individually and compared. Measurements in which particles were size selected before assessing their ice nucleation ability have been performed, such as those using continuous flow diffusion chambers as described in Koehler et al. (2010), Lüönd et al. (2010), Sullivan et al. (2010a), Welti et al. (2009), among others. However, a similar limitation to the cold plate experiments presents itself in which the freezing onsets of many droplets containing a range of particle sizes are averaged to find a frozen fraction curve. The resultant curves have potential internal and external variability embedded, with not enough information to disentangle them.

The argument for the existence of a species' specific critical area can be made for either a total number of particles in a specific size range or a total particle surface area. Assuming that a single species' surface area does not undergo intensive changes in its ice nucleation properties (such as chemical processing as discussed in Sullivan et al. (2010a, 2010b)) a cut-off critical size can be defined. Above this critical size the active site distribution is $\bar{g}$ while below it is some distribution of g's that can be sampled from $\bar{g}$. In one of the cases studied here in Fig. 5 for illite mineral particles the critical surface area was around 10^{-6} cm^2. This corresponds to a single spherical particle with an equivalent diameter of around 10 μm, a size cutoff that is quite atmospherically relevant (DeMott et al., 2010). The vast majority of the atmospheric particle number and surface area distributions are found at sizes smaller than 10 μm. Thus we conclude that for illite mineral particles, individual atmospheric particles will not contain the entire range of ice active site activity ($\bar{g}$) within that one particle, and each particle's ice nucleation ability is best described by an individual g distribution (that is a sub-sample of $\bar{g}$).

Application of Eq. (11) to find $A_{nucleation}$ for illite systems 6a (2.02×10^{-6} cm^2) and 5a (1.04×10^{-6} cm^2) from Broadley et al. (2012) gives insight into how the nucleating area is influencing the shape of the freezing curves. System 6a is where the critical area cutoff was found to occur while 5a started to exhibit the behavior of a broader freezing curve with a similar onset of freezing but with a diverging tail, indicating it is below the critical surface area. In Fig. 6 the average cumulative ice nucleating area computed from Eq. (11) is plotted against the critical contact angle range for the two systems. The total nucleating area at low contact angles is strikingly close between the two systems. This is because statistically the chance of possessing rare and highly active sites in an ensemble as large as system 5a is high as these occupy a small portion of the total particle area but have a substantial impact on the freezing behavior. This explains why the onset of freezing for the two curves is so similar. The diverging tail can be attributed to the divergence of the nucleating areas at higher contact angles in the critical contact angle range. The steeper rise of the average nucleating area of system 6a is due to its greater chance of possessing moderately strong active sites compared to system 5a due to the larger surface area present in 6a. This creates a larger spread in the freezing onset of droplets in system 5a after a few droplets initiated freezing in a similar manner to system 6a.

Deleted: higher

A similar nucleating area analysis was performed on the droplets containing Snomax and is shown in Fig. 12. The cumulative nucleating areas for the droplets with Snomax concentrations of 0.09 wt% and 0.08 wt% (red and green data in Fig. 8, respectively) are calculated and shown over the critical contact angle range with the same color scheme. Unlike the illite system, droplets containing Snomax exhibit a more straightforward trend in cumulative nucleating area vs. critical contact angle. The cumulative nucleating area is consistently smaller in the 0.08 wt% system compared to the 0.09 wt% experiment, indicating that as the particle surface area is reduced the strong nucleators are reduced uniformly over the critical contact angle range. This supports the idea that the range of active site activity is much smaller for this very ice active system. We propose that this is what explains the decrease in n_m with decreasing concentration observed in Fig. 5.

The implications of this analysis on the size dependence of g is that below the critical surface area particles may or may not possess freezing behavior similar to the particles above the critical area threshold. The broadening of the freezing curves in the systems analyzed here as the surface area is reduced is interpreted as heterogeneity in ice nucleating ability between the different particles (external variability) and not due to the internal variability within the individual particles themselves. While the broadness of the curves above the critical surface area can be attributed to internal variability, the additional broadness in curves below the critical area cutoff are a result of external variability.

More detailed analysis studying various atmospherically relevant ice nucleating particles needs to be done to shed light on whether a particle size cutoff corresponding to a critical area threshold can be used to describe the behavior of different species. This has important implications on whether one active site density function (i.e. $\bar{g}$ or n_s) is sufficient to accurately represent the species' ice nucleating properties in cloud or atmospheric models. If not, a more detailed parameterization resolving the multi-dimensional variability may be necessary, such as a series of g or $\bar{g}$ distributions. For illite it seems that external variability is dominant and thus one active site distribution or n_s parameterization does not properly represent the species' ice nucleation behavior. The critical area effect is even more substantial for cellulose and Snomax as their ice nucleating activity is much stronger than illite. However, if a system's global $\bar{g}$ distribution is obtained then its full ice nucleation behavior is contained within and can be successfully subsampled from $\bar{g}$. Cold plate droplet freezing measurements thus remain a crucial tool for unraveling the complex behavior of ice nucleating particles, particularly when a large particle concentration range is probed.

Cold plate experimental data potentially provides sufficient information to describe heterogeneous ice nucleation properties in cloud parcel and atmospheric models, however the analysis undertaken here suggests that retrieving one active site density parameterization (e.g. n_s) and applying it to all surface areas can result in misrepresenting the freezing behavior. When samples are investigated, probing a wide concentration range

Deleted: broadness

Deleted: 4a and 5a

Deleted: Fig. 5

Deleted: explained by the

Deleted: where the statistically significant

Deleted: lies for most

Deleted: larger

Deleted: material

Deleted: but it is a more involved process then

Deleted: (i.e. n_s)

Deleted: unconditionally.

enables the determination of both general active site density functions (e.g. $\bar{g}$) as well as the behavior of the species' under study at concentrations below the critical area threshold. Once this analysis is undertaken more comprehensive parameterizations can be retrieved as will be developed in the next section.

The critical area analysis carried out in this paper emphasizes the dangers in extrapolating the freezing behavior of droplets containing a large concentration of particle to droplets containing smaller concentrations or just individual particles. Applying a parameterization such as n_s directly to systems below the critical area threshold in a cloud parcel model for example yields large differences in the predictions of the freezing outcome of the droplet population. As the concentration of the species within the droplets was decreased in the cold plate freezing spectra considered here the actual freezing temperature curves diverged more and more from those predicted when the systems were assumed to be above the critical area. This led to significant changes in the retrieved n_s values, as shown in Figs. 4, 6b, and 7b. The large effects of concentration on the droplet freezing temperature can be directly observed in the frozen fraction curves plotted in Figs. 5, 6a, and 7a. Differences between observed frozen fraction curves and ones that assumed uniform active site density yielded errors in the temperature range the droplets froze over as well as the median droplet freezing temperature. Therefore, a cloud parcel model would be unable to accurately predict the freezing onset or the temperature range over which freezing occurs using a single n_s curve obtained from high concentration data. This has important consequences for the accurate simulation of the microphysical evolution of the cloud system under study such as the initiation of the Wegener–Bergeron–Findeisen and the consequent glaciation and precipitation rates (Ervens and Feingold, 2012; Ervens et al., 2011).

Figure 13 shows the range of n_s values for illite NX mineral compiled from seventeen measurements methods used by different research groups, the details of which are described by Hiranuma et al. (2014). The range of data is summarized into shaded sections to separate suspended droplet freezing techniques (such as a cold plate) from techniques where the material under investigation is aerosolized before its immersion freezing properties are assessed (such as the CFDC or AIDA cloud expansion chamber). The aerosol

Deleted: allows determining

Deleted: .

Deleted: droplet

Deleted: by Broadley et al. (2012),

Deleted: Figure

Deleted: . While a less than a factor of 2 change in n_s may seem insignificant, this does have significant effects on the predicted droplet freezing temperature given the exponential dependence of Eq. (18).

Deleted: experimental data from Broadley et al. (2012)

Deleted: Fig

Deleted: where such a difference in n_s values

Deleted: freezing curves spanning a broader

Deleted: and a different 50% frozen fraction point.

Deleted: huge

Deleted: on

techniques tend to produce higher retrieved n_s values than those obtained by the wet suspension methods. n_s data spanning a surface area range of about five orders of magnitude retrieved exclusively from both our cold plate measurements and Broadley et al. (2012) measurements are also plotted. Data presented in Fig. 8 that was consistent with a $\bar{g}$ treatment is plotted as n_s (gold and green rectangles). These two datasets along with what was identified as the critical area dataset from the Broadley et al. experiments follow a consistent n_s line that lies within the range of the suspended droplet techniques. The blue triangles are low surface area data points retrieved from dataset 4a from the Broadley et al. measurements. As was argued earlier, this system exhibits higher n_s values, an artifact of the increased active site density of some of the particles. While this data is retrieved with a cold plate, it falls within the range of the aerosolized methods where particle surface areas are small. Finally, more of the suspension method range of retrieved n_s can be spanned by data where the concentration saturation effect takes place. Data that exhibited this behavior from the CMU cold plate system (purple hexagons) and the Broadley et al. system (red and brown bowties) are plotted. This effect tends to underestimate n_s since additional material is added while the freezing behavior remains the same. Thus just by varying particle concentration and surface area of illite in the droplets, cold plate measurements can span the range of n_s values obtained by the various aerosol and wet suspension measurement methods. We emphasize again than n_s(T) should be the same for the same system, and this metric is often used as the major means to compare and evaluate different INP measurement methods.

Various research groups using wet suspension methods typically vary particle concentrations to span a wider range of measureable droplet freezing temperature (Broadley et al., 2012; Murray et al., 2012; Wright and Petters, 2013). Our analysis indicates that by doing so different n_s values are in fact retrieved, just due to changes in concentration. This highlights the importance of obtaining n_s values that overlap in temperature space, to evaluate if n_s is in fact consistent as concentration is changed. We therefore provide the critical area framework presented here whereby ice nucleating surface area dependence is more complex than depicted in traditional deterministic and stochastic models, as a potential source of the discrepancy in n_s values for the various measurement techniques. This commonly observed discrepancy in n_s between droplet suspension and

Formatted: Indent: First line: 0.2"

aerosol INP measurement methods is the subject of ongoing investigations, such as the INUIT project that is currently focusing on cellulose particles, a system we have included here. As the results from this multi-investigator project have not yet been published we cannot present them here. They show a similar trend as for the illite NX data, where the aerosol methods retrieve higher n_s values than the droplet suspension methods do. By changing particle in droplet concentration we can span much of the difference in n_s between the two groups of methods, as was shown for the illite NX measurements.

4 Application of the g parameterization to cloud models

Particle type-specific $\bar{g}$ distributions and critical areas can be used in larger cloud and atmospheric models to predict freezing onset and the rate of continued ice formation. The simplest parameterization is one that calculates the frozen fraction of droplets, F, for an atmospherically realistic system in which one ice nucleating particle is present in each supercooled droplet, the aerosol particle distribution is monodisperse (all particles therefore have the same surface area A), there is only one species present (therefore one $\bar{g}$ distribution is used), and the surface area of the individual particles is larger than that species' critical area. In this case Eq. (15) can be used:

$$F = 1 - \exp\left(-tA\int_0^{\pi} J(\theta,T)\overline{g(\theta)}d\theta\right) \qquad (15)$$

If the surface area of the individual particles is smaller than the critical area a modified version of Eq. (19) can be used instead:

$$F = 1 - \exp\left(-tA_c\int_0^{\pi} \left(J(\theta,T)\overline{g(\theta)}d\theta\right)h(A,T)\right) \qquad (19)$$

where $h(A,T)$ is an empirically derived parameterization that corrects for the individual particle surface areas of the considered monodisperse aerosol population being smaller than the critical area. Therefore $h(A_c,T) = 1$.

An example of retrieving values of $h(A,T)$ would be in correcting the solid line for system 4a (7.11×10^{-6} cm^2) to the dotted line in Fig. 5. The solid line is the basic use of Eq. (15) however it was shown that the considered experimentally retrieved freezing spectrum

Moved down [13]: . The frozen fraction curves produced from such an instrument do not provide enough information to associate the observed variability in ice nucleation ability to internal or external factors. However, future laboratory studies using the critical area-cold plate technique we have introduced here (e.g. Fig. 4) will provide new insight into the critical area thresholds of internal variability in ice active site ability for different species. This will produce more informed assumptions regarding the variability in ice nucleation properties observed through online field instruments, specifically when the measurements are made in conjunction with single particle chemical analysis techniques

Deleted: Systems that probe populations of droplets each containing one particle such as the CFDC are unable to probe a large particles-in-droplet concentration range but are powerful tools for the real-time investigations of ice nucleating particles at the realistic individual particle level (DeMott et al., 2010; Sullivan et al., 2010a; Welti et al., 2009)

Deleted: (Creamean et al., 2013; DeMott et al., 2003, 2010; Prather et al., 2013; Worringen et al., 2015). ... [19]

Formatted: Font:Not Bold

Formatted: Justified

Deleted: use

Deleted: 14

Deleted: $exp\left(-tA\int_0^{\pi} J(\theta,T)\overline{g(\theta)}d\theta\right)$

Deleted: 14

Formatted: Font:Times

Deleted: 14

Deleted: $F = 1 - exp\left(-tA_c\int_0^{\pi}\left(J(\theta,T)\overline{g(\theta)}d\theta\right)h(A,T)\right)$

Formatted: Font:Times

Deleted: 14

was below the critical area threshold. By taking the ratio of the dotted and solid lines values of h can be retrieved for that surface area at each temperature point.

Formatted: Font:Times, 12 pt

If the aerosol particle population is polydisperse and its size distribution can be expressed as a function of surface area, the frozen fraction can be written as:

$$F = \int_{A_i}^{A_f} \left[1 - \exp\left(-tA\int_{0}^{\pi}\left(J(\theta,T)\overline{g(\theta)}d\theta\right)h(A,T)dA\right)\right] \qquad (20)$$

where A_i and A_f are the minimum and maximum values of the surface areas of the aerosol particle distribution.

If the aerosol ice nucleating population is composed of multiple species, two $\bar{g}$ parameterizations can be formulated for the two cases of an internally mixed (every particle is composed of all the different species) and externally mixed (every particle is composed of just one species). For the case of an internally mixed system Eqs. (15), (19), and (20) can be applied with a $\bar{g}$ distribution that is the surface area weighted average of the $\bar{g}$ distributions of all the considered species. This can be expressed as:

Deleted: 14

$$\bar{g}_{average} = \frac{1}{A}\sum_{i=1}^{m} A_i\bar{g}_i \qquad (21)$$

where A_i is the surface area of the species i, $\bar{g}_i$ is the $\bar{g}$ distribution of the species i, and m is the total number of species. If the system is externally mixed, the frozen fraction can be expressed as:

$$F = \frac{1}{m}\sum_{i=1}^{m} F_i \qquad (22)$$

where F_i is the frozen fraction of droplets containing particles of species i and can be retrieved from Eq. (19) or (20).

5 Conclusions

Cold plate droplet freezing spectra were carefully examined to investigate a surface area dependence of ice nucleation ability whereby one active site density function such as n_s

Deleted: An ice active surface site-based stochastic model of heterogeneous ice nucleation with the unique feature of invoking a continuum assumption on the ice nucleating activity of a particle's surface was formulated. A particle specific property *g* that defines a distribution of local ice nucleation rates was then derived from the formulation. *g* is a Gaussian distribution of ice active site activity (contact angle, *θ*). By analyzing single particle-droplet cold plate freezing spectra, it was shown that internal variability of ice active site activity across a particle's surface can be a significant feature of a particle's observed ice nucleating ability. In addition to impacting the shape of a system's freezing temperature curve, internal variability can also affect a droplet's freezing sensitivity to time. A decrease in internal variability of active site ability, which can be caused by reducing particle-in-droplet concentrations, reduces the sensitivity of the freezing curve to time. Whether this impact is significant enough to merit the exclusion of stochastic effects in cloud and atmospheric models remains to be explored further.

... [20]

cannot be extrapolated from high particle surface area to low particle surface area conditions. A method based on the notion of a critical surface area threshold was presented. It is argued that a species' entire ice nucleating spectrum can be confined within a global probability density function $\bar{g}$. For a system, be it one particle or an ensemble of particles, to have a total surface area greater than the critical area is a question of whether the surface is large enough to express all the variability in that particle species' ice active surface site ability. By analyzing droplets containing illite minerals, MCC cellulose, and commercial Snomax bacterial particles, it was shown that freezing curves above a certain critical surface area threshold could be predicted directly from the global $\bar{g}$ distribution obtained from the high particle concentration data alone. The lower particle concentration freezing curves were accurately predicted by randomly sampling active site abilities (θ) from $\bar{g}$ and averaging their resultant freezing probabilities. This framework provides a new method for extrapolating droplet freezing temperature spectra from cold plate experimental data under high particle concentrations to atmospherically realistic dilute particle-droplet systems.

Deleted: in an attempt to disentangle the internal and external variability contributing to the shapes of the retrieved freezing temperature curves.

Deleted: statistically significant

Deleted: total particle

Deleted: By analyzing a case study on illite mineral particles from Broadley et al. (2012) it was shown that freezing curves above a certain critical surface area threshold can be accurately predicted directly from the global $\bar{g}$

Formatted: Justified

We found that the shifts to colder freezing temperatures caused by reducing the particle concentration or total surface area present in droplets cannot be fully accounted for by simply normalizing to the available surface area, as is done in the ice active site density (n_s) analysis framework. When the surface area is below the critical area threshold the retrieved values of n_s can increase significantly for the same particle species when the particle concentration is decreased. Above the critical area threshold the same n_s curves are retrieved when particle concentration is changed. Atmospheric cloud droplets typically contain just one particle each. Therefore, this effect of particle concentration on droplet freezing temperature spectra and the retrieved n_s values has important implications for the extrapolation of cold plate droplet freezing measurements to describe the ice nucleation properties of realistic atmospheric particles.

Systems that probe populations of droplets each containing one particle such as the CFDC are unable to probe a large particles-in-droplet concentration range but are powerful tools for the real-time investigations of ice nucleating particles at the realistic individual particle level (DeMott et al., 2010; Sullivan et al., 2010a; Welti et al., 2009). The frozen fraction curves produced from such an instrument do not provide enough information to

Moved (insertion) [13]

associate the observed variability in ice nucleation ability to internal or external factors. However, future laboratory studies using the critical area-cold plate technique we have introduced here (e.g. Fig. 4) will provide new insight into the critical area thresholds of internal variability in ice active site ability for different species. This will produce more informed assumptions regarding the variability in ice nucleation properties observed through online field instruments, specifically when the measurements are made in conjunction with single particle chemical analysis techniques (Creamean et al., 2013; DeMott et al., 2003, 2010; Prather et al., 2013; Worringen et al., 2015).

Atmospherically relevant particle sizes may very well fall below the critical area threshold for an individual particle, at least for some species such as illite mineral particles considered here. Therefore, average ice nucleation spectra or active site distributions such as n_s and $\bar{g}$ may not be applicable for representing the ice nucleation properties of particles in cloud and atmospheric models. However careful examination of the surface area dependence of ice nucleating ability of a species allows more accurate retrievals of active site density distributions that properly encompass this dependence.

Deleted: statistically significant

Deleted: A better representation is a distribution g that is retrieved from a random sampling procedure from the statistically significant global probability distribution function, $\bar{g}$. However to save large-scale models from the cost of generating these distributions for every particle, numerically retrieved correction factors denoted $h(A,T)$ can be used to transform the freezing curve of an ensemble of particle-droplet pairings obtained at particle concentrations above the critical area to atmospherically relevant low particle concentrations below this critical area

Acknowledgements

This research was partially supported by the National Science Foundation (Award CHE-1213718). The authors thank Dr. Paul DeMott for valuable discussions regarding an earlier version of this framework. Dr. Naruki Hiranuma at AIDA is acknowledged for providing us with the MCC cellulose sample, as part of the INUIT project.

6 References

Andreae, M. O. and Rosenfeld, D.: Aerosol–cloud–precipitation interactions. Part 1. The nature and sources of cloud-active aerosols, Earth Sci. Rev., 89(1-2), 13–41, 2008.

Baker, M. B. and Peter, T.: Small-scale cloud processes and climate., Nature, 451(7176), 299–300, doi:10.1038/nature06594, 2008.

Broadley, S. L., Murray, B. J., Herbert, R. J., Atkinson, J. D., Dobbie, S., Malkin, T. L., Condliffe, E. and Neve, L.: 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, 2012.

Cantrell, W. and Heymsfield, A.: Production of Ice in Tropospheric Clouds: A Review, Bull. Am. Meteorol. Soc., 86(6), 795–807, doi:10.1175/BAMS-86-6-795, 2005.

Creamean, J. M., Suski, K. J., Rosenfeld, D., Cazorla, A., Demott, P. J., Sullivan, R. C., White, A. B., Ralph, F. M., Minnis, P., Comstock, J. M., Tomlinson, J. M. and Prather, K. A.: Dust and biological aerosols from the Sahara and Asia influence precipitation in the western U.S., Science, 339(6127), 1572–1578, doi:10.1126/science.1227279, 2013.

DeMott, P. J., Cziczo, D. J., Prenni, A. J., Murphy, D. M., Kreidenweis, S. M., Thomson, D. S., Borys, R. and Rogers, D. C.: Measurements of the concentration and composition of nuclei for cirrus formation, Proc. Natl. Acad. Sci. U. S. A., 100(25), 14655–14660, 2003.

DeMott, P. J., Prenni, A. J., Liu, X., Kreidenweis, S. M., Petters, M. D., Twohy, C. H., Richardson, M. S., Eidhammer, T. and Rogers, D. C.: Predicting global atmospheric ice nuclei distributions and their impacts on climate, Proc. Natl. Acad. Sci. U. S. A., 107(25), 11217–11222, 2010.

Eidhammer, T., DeMott, P. J. and Kreidenweis, S. M.: A comparison of heterogeneous ice nucleation parameterizations using a parcel model framework, J. Geophys. Res., 114, D06202, doi:10.1029/2008jd011095, 2009.

Ervens, B. and Feingold, G.: On the representation of immersion and condensation freezing in cloud models using different nucleation schemes, Atmos. Chem. Phys., 12, 5807–5826, doi:10.5194/acp-12-5807-2012, 2012.

Ervens, B. and Feingold, G.: Sensitivities of immersion freezing: Reconciling classical nucleation theory and deterministic expressions, Geophys. Res. Lett., 40(12), 3320–3324, doi:10.1002/grl.50580, 2013.

Ervens, B., Feingold, G., Sulia, K. and Harrington, J.: The impact of microphysical parameters, ice nucleation mode, and habit growth on the ice/liquid partitioning in mixed-phase Arctic clouds, J. Geophys. Res., 116(D17), D17205, doi:10.1029/2011JD015729, 2011.

Fletcher, N. H.: Active Sites and Ice Crystal Nucleation, J. Atmos. Sci., 26(6), 1266–1271, doi:10.1175/1520-0469(1969)026<1266:ASAICN>2.0.CO;2, 1969.

Fornea, A. P., Brooks, S. D., Dooley, J. B. and Saha, A.: Heterogeneous freezing of ice on atmospheric aerosols containing ash, soot, and soil, J. Geophys. Res., 114, D13201, doi:10.1029/2009JD011958, 2009.

Hiranuma, N., Augustin-Bauditz, S., Bingemer, H., Budke, C., Curtius, J., Danielczok, A., Diehl, K., Dreischmeier, K., Ebert, M., Frank, F., Hoffmann, N., Kandler, K., Kiselev, A., Koop, T., Leisner, T., Möhler, O., Nillius, B., Peckhaus, A., Rose, D., Weinbruch, S., Wex, H., Boose, Y., DeMott, P. J., Hader, J. D., Hill, T. C. J., Kanji, Z. A., Kulkarni, G., Levin, E. J. T., McCluskey, C. S., Murakami, M., Murray, B. J., Niedermeier, D., Petters, M. D., O'Sullivan, D., Saito, A., Schill, G. P., Tajiri, T., Tolbert, M. A., Welti, A., Whale, T. F., Wright, T. P. and Yamashita, K.: A comprehensive laboratory study on the immersion freezing behavior of illite NX particles: a comparison of 17 ice nucleation measurement techniques, Atmos. Chem. Phys., 15(5), 2489–2518, doi:10.5194/acp-15-2489-2015, 2015.

Hoose, C. and Möhler, O.: Heterogeneous ice nucleation on atmospheric aerosols: a review of results from laboratory experiments, Atmos. Chem. Phys., 12(20), 9817–9854, doi:10.5194/acp-12-9817-2012, 2012.

Hoose, C., Kristjánsson, J. E., Chen, J.-P. and Hazra, A.: A Classical-Theory-Based Parameterization of Heterogeneous Ice Nucleation by Mineral Dust, Soot, and Biological Particles in a Global Climate Model, J. Atmos. Sci., 67(8), 2483–2503, doi:10.1175/2010JAS3425.1, 2010.

Koehler, K. a., Kreidenweis, S. M., DeMott, P. J., Petters, M. D., Prenni, a. J. and Möhler, O.: Laboratory investigations of the impact of mineral dust aerosol on cold cloud formation, Atmos. Chem. Phys., 10(23), 11955–11968, doi:10.5194/acp-10-11955-2010, 2010.

Koop, T., Luo, B. P., Tsias, A. and Peter, T.: Water activity as the determinant for homogeneous ice nucleation in aqueous solutions, Nature, 406(6796), 611–614, 2000.

Liu, X. and Penner, J. E.: Ice nucleation parameterization for global models, Meteorol. Zeitschrift, 14(4), 499–514, 2005.

Lüönd, F., Stetzer, O., Welti, A. and Lohmann, U.: Experimental study on the ice nucleation ability of size-selected kaolinite particles in the immersion mode, J. Geophys. Res., 115(D14), 1–14, doi:10.1029/2009JD012959, 2010.

Marcolli, C., Gedamke, S., Peter, T. and Zobrist, B.: Efficiency of immersion mode ice nucleation on surrogates of mineral dust, Atmos. Chem. Phys., 7(19), 5081–5091, 2007.

Meyers, M. P., DeMott, P. J. and Cotton, W. R.: New primary ice-nucleation parameterizations in an explicit cloud model, J. Appl. Meteorol., 31(7), 708–721, 1992.

Mülmenstädt, J., Sourdeval, O., Delanoë, J. and Quaas, J.: Frequency of occurrence of rain from liquid-, mixed-, and ice-phase clouds derived from A-Train satellite retrievals, Geophys. Res. Lett., 42(15), 6502–6509, doi:10.1002/2015GL064604, 2015.

Murray, B. J., Broadley, S. L., Wilson, T. W., Atkinson, J. D. and Wills, R. H.: Heterogeneous freezing of water droplets containing kaolinite particles, Atmos. Chem. Phys., 11(9), 4191–4207, doi:10.5194/acp-11-4191-2011, 2011.

Murray, B. J., O'Sullivan, D., Atkinson, J. D. and Webb, M. E.: Ice nucleation by particles immersed in supercooled cloud droplets., Chem. Soc. Rev., 41(19), 6519–54, doi:10.1039/c2cs35200a, 2012.

Niedermeier, D., Shaw, R. a., Hartmann, S., Wex, H., Clauss, T., Voigtländer, J. and Stratmann, F.: Heterogeneous ice nucleation: exploring the transition from stochastic to singular freezing behavior, Atmos. Chem. Phys., 11(16), 8767–8775, doi:10.5194/acp-11-8767-2011, 2011.

Phillips, V. T. J., DeMott, P. J. and Andronache, C.: An Empirical Parameterization of Heterogeneous Ice Nucleation for Multiple Chemical Species of Aerosol, J. Atmos. Sci., 65(9), 2757–2783, doi:10.1175/2007JAS2546.1, 2008.

Phillips, V. T. J., Demott, P. J., Andronache, C., Pratt, K. A., Prather, K. A., Subramanian, R. and Twohy, C.: Improvements to an Empirical Parameterization of Heterogeneous Ice Nucleation and Its Comparison with Observations, J. Atmos. Sci., 70(2), 378–409, doi:10.1175/JAS-D-12-080.1, 2013.

Prather, K. A., Bertram, T. H., Grassian, V. H., Deane, G. B., Stokes, M. D., Demott, P. J., Aluwihare, L. I., Palenik, B. P., Azam, F., Seinfeld, J. H., Moffet, R. C., Molina, M. J., Cappa, C. D., Geiger, F. M., Roberts, G. C., Russell, L. M., Ault, A. P., Baltrusaitis, J., Collins, D. B., Corrigan, C. E., Cuadra-Rodriguez, L. A., Ebben, C. J., Forestieri, S. D., Guasco, T. L., Hersey, S. P., Kim, M. J., Lambert, W. F., Modini, R. L., Mui, W., Pedler, B. E., Ruppel, M. J., Ryder, O. S., Schoepp, N. G., Sullivan, R. C. and Zhao, D.: Bringing the ocean into the laboratory to probe the chemical complexity of sea spray aerosol., Proc. Natl. Acad. Sci. U. S. A., 110(19), 7550–5, doi:10.1073/pnas.1300262110, 2013.

Pruppacher, H. R. and Klett, J. D.: Microphysics of Clouds and Precipitation, edited by R. D. Rosen, Kluwer Academic Publishers., 1997.

Rosenfeld, D., Lohmann, U., Raga, G. B., O'Dowd, C. D., Kulmala, M., Fuzzi, S., Reissell, A. and Andreae, M. O.: Flood or drought: how do aerosols affect precipitation?, Science, 321(5894), 1309–13, doi:10.1126/science.1160606, 2008.

Sullivan, R. C., Miñambres, L., DeMott, P. J., Prenni, A. J., Carrico, C. M., Levin, E. J. T. and Kreidenweis, S. M.: Chemical processing does not always impair heterogeneous ice nucleation of mineral dust particles, Geophys. Res. Lett., 37(24), L24805, doi:10.1029/2010GL045540, 2010a.

Sullivan, R. C., Petters, M. D., DeMott, P. J., Kreidenweis, S. M., Wex, H., Niedermeier, D., Hartmann, S., Clauss, T., Stratmann, F., Reitz, P., Schneider, J. and Sierau, B.: Irreversible loss of ice nucleation active sites in mineral dust particles caused by sulphuric acid condensation, Atmos. Chem. Phys., 10, 11471–11487, 2010b.

Vali, G.: Freezing rate due to heterogeneous nucleation, J. Atmos. Sci., 51(13), 1843–1856, 1994.

Vali, G.: Repeatability and randomness in heterogeneous freezing nucleation, Atmos. Chem. Phys., 8(16), 5017–5031, 2008.

Vali, G.: Interpretation of freezing nucleation experiments: singular and stochastic; sites and surfaces, Atmos. Chem. Phys., 14(11), 5271–5294, doi:10.5194/acp-14-5271-2014, 2014.

Vali, G. and Stransbury, E. J.: Time Dependant Charactirisitcs of the Heterogeneous Nucleation of Ice, Can. J. Phys., 44(3), 477–502, 1966.

Vali, G., DeMott, P. J., Möhler, O. and Whale, T. F.: Technical Note: A proposal for ice nucleation terminology, Atmos. Chem. Phys., 15(18), 10263–10270, doi:10.5194/acp-15-10263-2015, 2015.

Welti, A., Lund, F., Stetzer, O. and Lohmann, U.: Influence of particle size on the ice nucleating ability of mineral dusts, Atmos. Chem. Phys., 9(18), 6705–6715, 2009.

Wex, H., Augustin-Bauditz, S., Boose, Y., Budke, C., Curtius, J., Diehl, K., Dreyer, A., Frank, F., Hartmann, S., Hiranuma, N., Jantsch, E., Kanji, Z. A., Kiselev, A., Koop, T., Möhler, O., Niedermeier, D., Nillius, B., Rösch, M., Rose, D., Schmidt, C., Steinke, I. and Stratmann, F.: Intercomparing different devices for the investigation of ice nucleating particles using Snomax® as test substance, Atmos. Chem. Phys., 15(3), 1463–1485, doi:10.5194/acp-15-1463-2015, 2015.

Wheeler, M. J. and Bertram, A. K.: Deposition nucleation on mineral dust particles: A case against classical nucleation theory with the assumption of a single contact angle, Atmos. Chem. Phys., 12(2), 1189–1201, doi:10.5194/acp-12-1189-2012, 2012.

Worringen, A., Kandler, K., Benker, N., Dirsch, T., Mertes, S., Schenk, L., Kästner, U., Frank, F., Nillius, B., Bundke, U., Rose, D., Curtius, J., Kupiszewski, P., Weingartner, E., Vochezer, P., Schneider, J., Schmidt, S., Weinbruch, S. and Ebert, M.: Single-particle characterization of ice-nucleating particles and ice particle residuals sampled by three different techniques, Atmos. Chem. Phys., 15(8), 4161–4178, doi:10.5194/acp-15-4161-2015, 2015.

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

Wright, T. P., Petters, M. D., Hader, J. D., Morton, T. and Holder, A. L.: Minimal cooling rate dependence of ice nuclei activity in the immersion mode, J. Geophys. Res. Atmos., 118(18), 10,535–10,543, doi:10.1002/jgrd.50810, 2013.

Zobrist, B., Koop, T., Luo, B. P., Marcolli, C. and Peter, T.: Heterogeneous ice nucleation rate coefficient of water droplets coated by a nonadecanol monolayer, J. Phys. Chem. C, 111(1), 2149–2155, doi:10.1021/jp066080w, 2007.

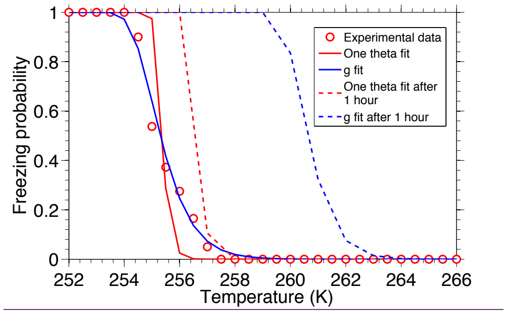

Figure 1. Experimentally determined freezing probabilities and fits from freezing of a droplet containing a single large ~300 μm diameter volcanic ash particle, from Fornea et al. (2009). Red dots are experimental freezing probabilities retrieved from repeated droplet freezing measurements. The red line is a fit to the data using classical nucleation theory and the assumption of a single contact angle (θ). The blue line is a fit to the data using the g framework developed here, which describes a Gaussian distribution of θ. The g fit has a least square error sum of 0.0197, μ = 1.65, and σ = 0.135. The dotted red line is the simulated freezing curve resulting from a single θ distribution after the droplets are held at the same temperature for 1 hour. The dotted blue line is the freezing curve from a multiple θ distribution described by g after the same temperature hold simulation.

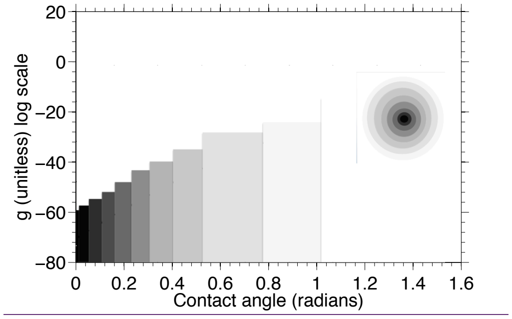

Figure 2. Upper right inset displays the distribution of ice nucleation activity (contact angle, θ) for a representative spectrum of a particle's ice nucleating activity. The less active (white) surface sites have more surface coverage while the more active (black) surface sites have less coverage. The probability distribution function for the g distribution (μ = 1.65, and σ = 0.135, retrieved in Section 3.1) ascent in log space is plotted with numerical bins. The darker colors are used to highlight the stronger ice nucleating activity at smaller contact angles (θ).

Deleted: Fornea et al. (2009)

Deleted:

Deleted: effective ice active surface site

Deleted: an

Deleted: particle

Deleted: a sample

Deleted: (mode = μ, standard deviation = σ)

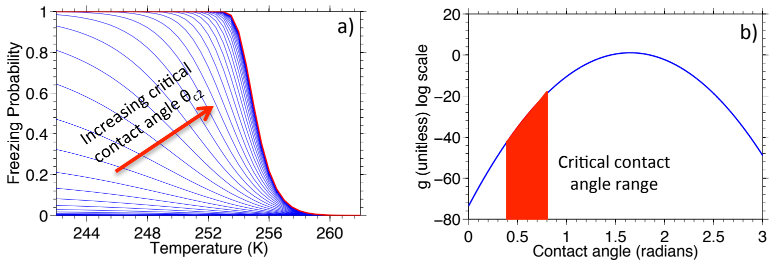

Figure 3. **Left (a):** Identifying the critical contact angle range. The thin blue curves are retrieved from application of the simplified Eq. (10), which approximates the freezing probability by integrating over a smaller contact angle range, $[\theta_{c_1}, \theta_{c_2}]$, while the thick red curve is obtained from application of the complete Eq. (7), which integrates over the full contact angle range. Both approaches use the same g distribution retrieved for the case example in section 3.1 with $\mu = 1.65$, and $\sigma = 0.135$. **Right (b):** The g distribution from the case example in Section 3.1 plotted in log scale and showing the critical contact angle range retrieved in Section 3.2 ($\theta_{c1} \approx 0.4$ rad and $\theta_{c2} \approx 0.79$) in red.

Formatted: Font:Bold

Formatted: Centered

Deleted: <sp>

Formatted: Font:Bold

Deleted: Both approaches use the same sample *g* distribution

Formatted: Font:Bold

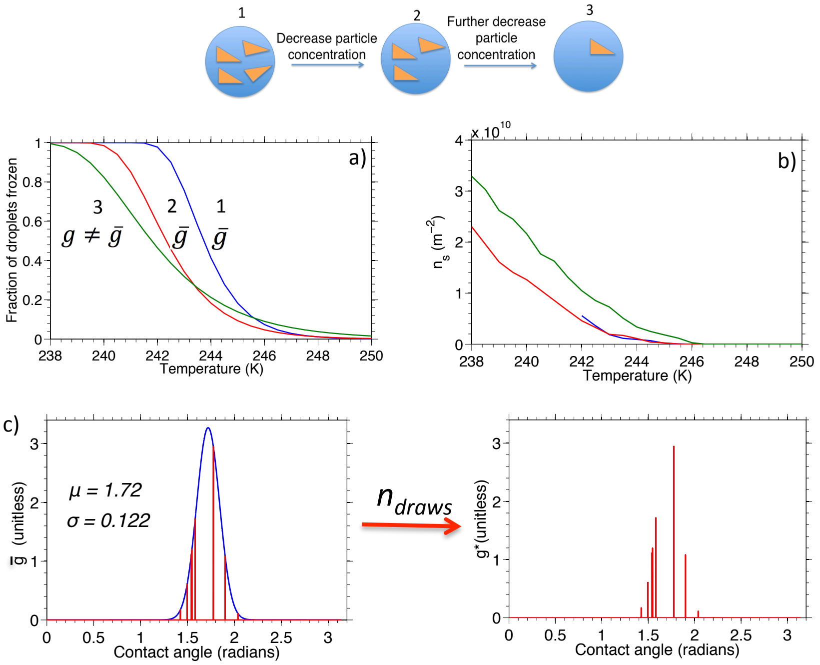

Figure 4. Top: Schematic summarizing the procedure for determining the critical area. **Left** (a): The frozen fraction freezing curves shift to lower temperatures initially due solely to the decrease in total surface area of the ice nucleating particles (curves 1 & 2). As the total surface area of the particles is decreased below the critical area threshold ($g \neq \bar{g}$) the slope of the freezing curve also broadens because the effective distribution of ice nucleating sites has changed – more external variability has been introduced (curve 3). **Right** (b): Ice active site density (n_s) retrieved from the frozen fraction plots on the left for the same three particle concentration systems. Above the critical area limit ($g = \bar{g}$) the two n_s curves are essentially the same, but below the critical area threshold ($g \neq \bar{g}$) n_s increases, even though the same particle species was measured in all three experiments. These exemplary frozen fraction and n_s curves were produced by fitting a $\bar{g}$ distribution to droplet freezing measurements of illite mineral particles from Broadley et al. (2012). **Bottom (c):** Schematic summarizing how g^* is retrieved from $\bar{g}$ using n_{draws}. In each draw a random contact angle from the full range of contact angles [0, π] is chosen after which the value of g^* at that contact angle (right) is assigned the value of $\bar{g}$ at the same contact angle (left).

Deleted: :

Deleted: :

Deleted: (2012).

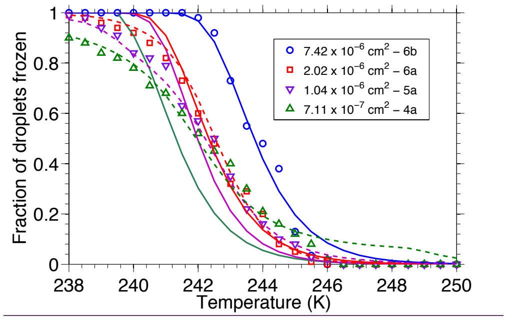

Figure 5. Experimental freezing curves for different surface area concentrations of illite mineral powder immersed in 10-20 μm diameter water droplets taken from Broadley et al. (2012) (circles). Lines are modeled predictions of the same data using the g^* distribution method. Solid lines are produced directly from the global $\bar{g}$ distribution first obtained from the high concentration system. The dashed lines are obtained by randomly sub-sampling the global $\bar{g}$ distribution to obtain g^* and following a surface area correction, as described in the text.

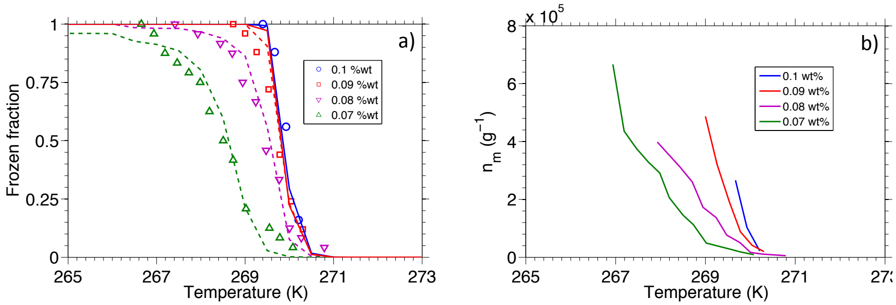

Figure 6. Left (a): Experimental freezing curves for different mass concentrations of commercial Snomax powder immersed in 200-300 μm diameter water droplets obtained using the CMU cold plate (circles). Solid lines are fits produced from randomly sampling from the $\bar{g}$ distribution retrieved from the highest concentration freezing curve (0.1 %wt). Dashed lines are fits produced from randomly sampling from the $\bar{g}$ distribution and a surface area correction. The second highest concentration freezing curve (0.09 %wt) is used to confirm the critical area threshold had been exceeded. **Right (b):** Ice active site density (n_m) retrieved from the frozen fraction data on the left. A trend of decreasing n_m with decreasing concentration is observed for the droplets containing Snomax.

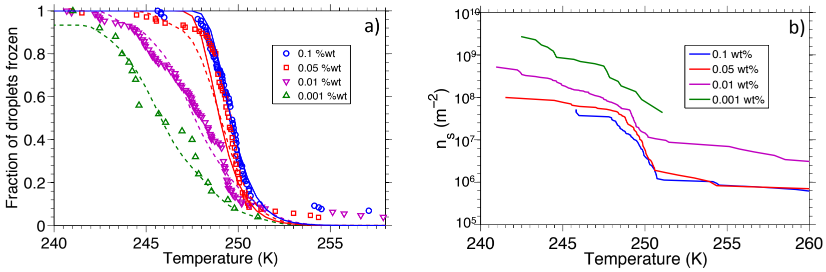

Figure 7. **Left (a)**: Experimental freezing curves for different mass concentrations of MCC cellulose powder immersed in 500-600 µm diameter water droplets obtained using the CMU cold plate (circles). Dashed lines are fits produced from randomly sampling from the $\bar{g}$ distribution retrieved from the highest concentration freezing curve (0.1 wt%, blue solid line) and a surface area correction. The second highest concentration freezing curve (0.05 wt%, red) is used to confirm the critical area threshold was exceeded. **Right (b)**: Ice active site density (n_s) retrieved from the frozen fraction data on the left. A trend of increasing n_s with decreasing concentration is observed.

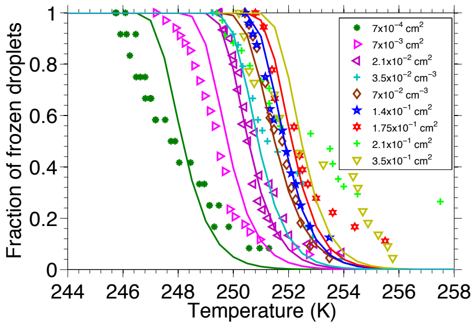

Figure 8. Experimental freezing curves for different mass concentrations of illite NX powder immersed in 500-600 µm diameter water droplets obtained using the CMU cold plate (circles). The solid lines are the predicted frozen fractions based on the $\bar{g}$ distribution retrieved from the Broadley et al. (2012) data and a surface area correction. A concentration saturation effect appears to be present, whereby the blue, red, and gold experimental data points overlap despite being at different concentrations.

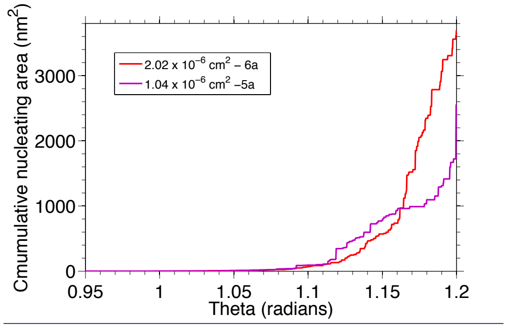

Figure 9. Cumulative ice nucleating surface areas from application of Eq. (11) to modeled average *g* distributions from systems 6a (red) and 5a (purple) in Fig. 5, taken from cold plate measurements of illite in droplets from Broadley et al. (2012), plotted against the critical contact angle range. At low contact angles the two systems have close total nucleating surface areas. This explains the similar onset of freezing before the eventual divergence at lower temperature (larger contact angle).

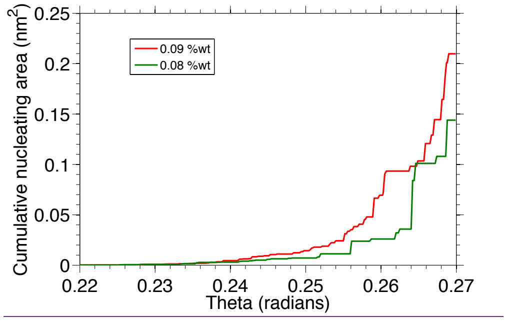

Figure 10. Cumulative ice nucleating surface areas from application of Eq. (11) to modeled average *g* distributions from droplets containing 0.09 wt% Snomax (red) and 0.08 wt% Snomax (green) in Fig. 8 plotted against the critical contact angle range. This system does not exhibit similar nucleating areas at low contact angles, and thus does not show an increase in n_s with decreasing concentration (or surface area).

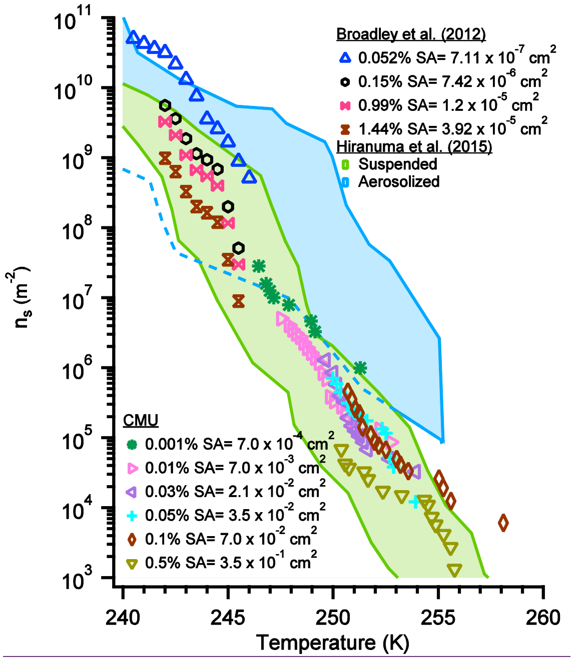

Figure 11. Range of n_s values for illite NX mineral dust compiled from seventeen measurement methods used by different research groups, the details of which are described by Hiranuma et al. (2015). The range of data is summarized into shaded sections to separate suspended droplet techniques (such as the cold plate) from techniques where the material under investigation is aerosolized before immersion freezing analysis. Data from both the Broadley et al. (2012) and the CMU cold plate systems are also plotted to show how much of the range can be spanned via the critical area effect (blue triangles) and the concentration saturation effect (purple hexagons and red and brown bow ties).