

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.”

²Laboratory 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, then 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 $g(\theta)$ 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 $\theta_{c1} = 0$ 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 $300 \mu\text{m}$ and a cooling rate of 10 K/min $\theta_{c1} \approx 0.4 \text{ rad}$ and $\theta_{c2} \approx 0.79 \text{ rad}$."

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 $g(\theta)$ 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 $\theta_{c1} \neq 0$, 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 ($1.04 \times 10^{-6} \text{ cm}^2 - 5a$; and $7.11 \times 10^{-7} \text{ cm}^2 - 4a$) 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 $1.04 \times 10^{-6} \text{ cm}^2$ (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 ($7.11 \times 10^{-7} \text{ cm}^2 - 4a$) 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 $n_s(T)$ 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 $n_s(T)$ 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 divergence 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 concentration. 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 appear 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 n_s 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 n_{draw} ?

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 $[0, \pi]$, and the value of active site distribution g^* for the particle i being sampled for at θ_r is assigned the value of $\overline{g(\theta_r)}$:

$$(g_i^*(\theta_r, n_{draw})) = \overline{g(\theta_r)} \quad (16)$$

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:

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

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 $n_s(T)$ 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 $\bar{g}$ -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 $g(\theta)$ 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 $\bar{g}$ -bar function, i.e. for $0 < \theta < \pi$?

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 $[0, \pi]$, and the value of active site distribution g^* for the particle i being sampled for at θ_r is assigned the value of $\frac{g(\theta_r)}{g(\theta_r)}$.”

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 (θ_{c1} and θ_{c2}) 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 θ_{c2} is less interesting as it corresponds to a high number of possible occurrences, while values near θ_{c1} 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 $\bar{g}$. The method followed in the paper for determining $\bar{g}$ and the critical contact angles θ_{c1} and θ_{c2} appears to consist of fitting Eq. 15 to the $F(T)$ 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 θ_{c1} and θ_{c2} can be examined by looking at evidence in terms of spectra of INP concentrations either in terms of $n_s(T)$ or $K(T_c)$. 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 $n_s(T)$ or $K(T_c)$ 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 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 $n_s(T)$ or $K(T_c)$ 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 $J(\theta)$ does not vary much in shape. Hence the dominant variations in the integral comes from $g(\theta)$ and that quantity is a measure of the frequency of different sites just as $n_s(T)$ or $K(T_c)$ 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 be 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.