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

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- 4 Hassan Beydoun¹, Michael Polen¹, and Ryan C. Sullivan^{1,*}
- 6 [1] Center for Atmospheric Particle Studies, Carnegie Mellon University, Pittsburgh PA
- 8 Correspondence to: R. C. Sullivan (rsullivan@cmu.edu)
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13 Abstract

14 Heterogeneous ice nucleation remains one of the outstanding problems in cloud physics 15 and atmospheric science. Experimental challenges in properly simulating particle-16 induced freezing processes under atmospherically relevant conditions have largely 17 contributed to the absence of a well-established parameterization of immersion freezing 18 properties. Here we formulate an ice active surface site based stochastic model of 19 heterogeneous freezing with the unique feature of invoking a continuum assumption on 20 the ice nucleating activity (contact angle) of an aerosol particle's surface, that requires no 21 assumptions about the size or number of active sites. The result is a particle specific 22 property g that defines a distribution of local ice nucleation rates. Upon integration this 23 yields a full freezing probability function for an ice nucleating particle.

24 Current cold plate droplet freezing measurements provide a valuable and inexpensive 25 resource for studying the freezing properties of many atmospheric aerosol systems. We 26 apply our q framework to explain the observed dependence of the freezing temperature 27 of droplets in a cold plate on the concentration of the particle species investigated. 28 Normalizing to the total particle mass or surface area present to derive the commonly 29 used ice nuclei active surface (INAS) density (n_s) often cannot account for the effects of 30 particle concentration, yet concentration is typically varied to span a wider measureable 31 freezing temperature range. A method based on determining what is denoted an ice 32 nucleating species' specific critical surface area is presented that explains the 33 concentration dependence as a result of increasing the variability in ice nucleating active 34 sites between droplets. By applying this method to experimental droplet freezing data from four different systems we demonstrate its ability to interpret immersion freezing
 temperature spectra of droplets containing variable particle concentrations.

3 It is shown that general active site density functions such as the popular n_s 4 parameterization cannot be reliably extrapolated below this critical surface area threshold 5 to describe freezing curves for lower particle surface area concentrations. Freezing curves 6 obtained below this threshold translate to higher n_s values, while the n_s values are 7 essentially the same from curves obtained above the critical area threshold; n_s should 8 remain the same for a system as concentration is varied. However, we can successfully 9 predict the lower concentration freezing curves, which are more atmospherically relevant, 10 through a process of random sampling from g distributions obtained from high particle 11 concentration data. Our analysis is applied to cold plate freezing measurements of 12 droplets containing variable concentrations of particles from NX illite minerals, MCC 13 cellulose, and commercial Snomax bacterial particles. Parameterizations that can predict 14 the temporal evolution of the frozen fraction of cloud droplets in larger atmospheric 15 models are also derived from this new framework.

16

17 **1** Introduction

18 Above water's homogenous freezing temperature near -38 °C supercooled cloud 19 droplets can only crystallize on a rare subset of atmospheric aerosol particles termed ice 20 nucleating particles (INP) (Baker and Peter, 2008; Vali et al., 2015). The scarcity of these 21 particles directly affects cloud structure, evolution, and precipitation via inducing the 22 Wegener-Bergeron-Findeisen (WBF) process, where ice crystals rapidly grow at the 23 expense of liquid cloud droplets in mixed-phase clouds. Ice nucleation thus plays a 24 crucial role in determining cloud evolution, lifetime, and properties, creating important 25 feedbacks between aerosols, clouds, precipitation, and climate (Pruppacher & Klett, 26 1997; Rosenfeld et al., 2008). As a result, most precipitation over land is induced by 27 cloud glaciation (Cantrell and Heymsfield, 2005; Mülmenstädt et al., 2015). Accurate 28 representation of cirrus and mixed phase clouds in atmospheric models therefore 29 necessitates properly parameterizing the heterogeneous ice nucleation process (DeMott et 30 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).

3 Great challenges in observing the actual heterogeneous ice nucleation nanoscale 4 process is the main culprit impeding the formulation of a consistent and comprehensive 5 framework that can accurately and efficiently represent heterogeneous ice nucleation in 6 atmospheric models (Cantrell and Heymsfield, 2005); we still do not understand what 7 precisely controls the ice nucleation ability of ice active surface sites that catalyze ice 8 embryo formation. There are currently two competing views on the dominant factors that 9 control the heterogeneous ice nucleation process, the stochastic versus deterministic 10 framework (Niedermeier et al., 2011; Vali, 2014). The stochastic framework assumes that 11 freezing occurs randomly across a particle's surface and can be constrained with a 12 temperature dependent nucleation rate (Pruppacher and Klett, 1997). This effectively 13 yields time dependent freezing and an element of non-repeatability (Vali, 2008). On the 14 other hand in the deterministic framework ice nucleation is dictated by ice active surface 15 sites (Fletcher, 1969; Levine, 1950; Meyers et al., 1992; Sear, 2013). Each active site has 16 a characteristic critical freezing temperature, with the site with the highest critical 17 temperature always initiating crystallization instantly (Vali, 2008). Careful examination 18 of the experimental results published by Vali (2008) indicates that the very nature of the 19 process need not be in contention. These results suggest that there is a strong spatial 20 preference on where nucleation occurs, supporting a model of discrete active sites. 21 However, temperature fluctuations still occur indicating that a stochastic element also 22 exists. Considering several decades of experimental work and theoretical considerations 23 (Ervens and Feingold, 2013; Murray et al., 2012; Vali and Stransbury, 1966; Vali, 1994, 24 2014; Wright and Petters, 2013; Wright et al., 2013), the role of time has been 25 determined to play a much weaker role than temperature does. It remains to be seen 26 whether the difference is significant enough for time-dependent freezing to be completely 27 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,

2 2012), and also reflects our fundamental understanding of this nucleation process. Ervens & 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.

8 A new parameterization, based on classical nucleation theory, is formulated in this 9 paper. The new framework is stochastic by nature to properly reflect the randomness of 10 ice embryo growth and dissolution, and assumes that an ice nucleating particle can 11 exhibit variability in active sites along its surface, what will be referred to as internal 12 variability, and variability in active sites between other particles of the same species, 13 what will be referred to as external variability. A new method is presented to analyze and 14 interpret experimental data from the ubiquitous droplet freezing cold plate method using 15 this framework, and parameterize these experimental results for use in cloud parcel 16 models. New insights into the proper design of cold plate experiments and the analysis of 17 their immersion freezing datasets to accurately describe the behavior of atmospheric ice 18 nucleating particles are revealed. Based on experimental observations and the new 19 framework we argue that active site schemes that assume uniform active site density such 20 as the popular n_s parameterization – a deterministic framework that assigns an active site 21 density as a function of temperature (Hoose et al., 2008; Vali, 1971) - are unable to 22 consistently describe freezing curves over a wide surface area range. This shortcoming is 23 argued to be one of the causes of the discrepancies in retrieved n_s values of the same ice 24 nucleating species using different measurement methods and particle in droplet 25 concentrations (Emersic et al., 2015; Hiranuma et al., 2015a; Wex et al., 2015).

26

27 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:

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

(1)

4 where J is the ice nucleation rate and has units of freezing events/(time \times volume). ΔG is 5 the energy barrier to crystallization from liquid water as defined in Pruppacher & Klett 6 (1997) and Zobrist et al. (2007). T is temperature, k the Boltzmann constant, and C is a 7 constant. For typical cloud droplet volumes, a temperature of about -38 °C is typically 8 required for the homogeneous ice nucleation rate to become significantly fast such that 9 freezing occurs within minutes or less. At temperatures between -38 and 0 °C a catalyst is 10 required to initiate freezing of cloud droplets. Certain rare aerosol particles - ice 11 nucleating particles – can act as these catalysts and induce heterogeneous ice nucleation 12 in the atmosphere.

13 In expanding to heterogeneous ice nucleation the simplest approach is to assume that 14 instead of ice germ formation occurring randomly throughout a bulk volume of 15 supercooled water, ice nucleation is initiated on a surface. The surface reduces the 16 nucleation energy barrier ΔG by a factor f, dependent on the contact angle between liquid 17 water and the material. The contact angle θ [0, π] is actually a proxy for the water-18 surface interaction system, with smaller values of θ indicating that the surface is a better 19 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 20 21 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 22 23 heterogeneous ice nucleation rate for a volume of water containing a total surface area of 24 ice nucleating particles (INP) therefore can be defined as (Pruppacher and Klett, 1997):

25
$$J(T) = C \exp\left(-\frac{f(\theta)\Delta G}{kT}\right)$$
(2)

26 where J in this case would be expressed as freezing events/(time \times 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 some time *t* resembles a first order chemical decay (Pruppacher and Klett, 1997; Vali, 2008):

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

7 where N_f is the fraction of droplets frozen after time *t* at temperature *T*, *N* is the total 8 number of particle-droplet pairings and *A* is the surface area of each individual ice 9 nucleating particle (assumed to be the same for all particles). Furthermore, a probability 10 of ice nucleation, P_f , at the single droplet-particle level can be defined as:

$$P_f = 1 - \exp(-JAt) \tag{4}$$

12

13 3 Formulation of g: a continuum approach of active site activity to describe 14 heterogeneous ice nucleation

15 Given the large variability in particle surface composition and structure across any one 16 particle, which in turn determines the activity (or contact angle, θ) of a potential ice 17 nucleating site, a different approach is to assume that the heterogonous nucleation rate 18 will vary along the particle-droplet interface. Since the critical nucleation area ($\sim nm^2$) is much smaller than the total particle area ($\sim \mu m^2$), we apply a continuum assumption for 19 20 the ice active site activity (θ) available across a particle's surface without assumptions 21 about the size or number of active sites per particle surface area. The new resulting 22 probability of freezing is:

23
$$P_f = 1 - \exp\left(-t\int J\,dA\right) \tag{5}$$

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:

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

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

3
$$P_f = 1 - \exp\left(-tA \int_0^{\pi} J(\theta)g(\theta)d\theta\right)$$
(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.

11 In this work the *internal* variability of an individual ice nucleating particle expresses 12 the heterogeneity of its ice nucleating surface. A wider (larger σ) g distribution describes 13 a greater particle internal variability of ice active surface site properties or contact angles 14 present on that one particle. This is in contrast to the external variability of an ice 15 nucleating species, which expresses how diverse a population of particles is in their ice 16 nucleation activities. External variability accounts for differences in the q distributions of 17 individual particles between particles of the same type (such as particles composed of the 18 same mineral phases).

19 We hypothesize that experimentally probed systems can be interpreted as exhibiting 20 internal and external variability based on differences in freezing temperatures of different 21 droplets containing the same material, i.e. the freezing temperature spectrum of a droplet 22 array. The model will be shown to provide a conceptual explanation of what this 23 variability, be it internal or external, stems from. We provide this as a potential 24 explanation for discrepancies in the measured values of the popular deterministic scheme 25 n_s (Hoose and Möhler, 2012; Vali, 2014) for different particle concentrations and 26 consequently different measurements methods. In the following sections the model is 27 developed further to shed light on the impact of the q 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.

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4 **3.1** Internal variability and its impact on time dependent freezing

5 To explore the importance of accounting for ice nucleating variability along a single 6 particle's surface (internal variability) we examined the temperature dependent freezing 7 curves of droplets with single large ash particles immersed in them from Fornea et al. 8 (2009). Their experiments were performed with cooling rates of 1 °C/min. Figure 1 9 displays their experimental data (red dots), a single contact angle (θ) fit to their data (red 10 solid line) that assumes no internal variability, and a g distribution fit using multiple θ s 11 (solid blue line) that allows for internal variability. Fornea et al. retrieved their 12 experimental data points by averaging the observed freezing temperature of the same ash 13 particle-droplet pair after multiple freezing cycles. The averaged values are denoted 14 freezing probabilities since they represent the chance of freezing occurring at that 15 temperature. The ash particle diameter was around 300 μ m, clearly much larger than 16 atmospheric particle sizes.

17 To fit a g distribution to an empirical freezing curve, a least square error approach is 18 implemented. A matrix of freezing probabilities is generated for all possible g19 distributions. If the experimental freezing curve has been retrieved from experiments in 20 which the temperature is dictated by a non-constant cooling rate, an expression that 21 satisfies this condition must be used:

22
$$P_f = 1 - \exp\left(-A \int_0^t \int_0^\pi J(T(t), \theta) g(\theta) d\theta dt\right)$$
(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:

25
$$P_f = 1 - \exp\left(-\frac{A}{\dot{T}} \int_{T_i}^{T_f} \int_{0}^{\pi} J(T,\theta)g(\theta)d\theta dT\right)$$
(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.

3 The g fit performs much better in capturing the behavior of the observed freezing 4 temperature spectrum in Fig. 1, as expected given the greater degrees of freedom allowed 5 for the multiple θ fit. The single θ fit has a steeper dependence on temperature; the 6 double exponential temperature dependence of the freezing probability in Eq. (4) (J is an 7 exponential function of temperature in itself as can be seen in Eq. (2)) results in an 8 approximately temperature step function. The diversity of nucleating ability on the 9 particle surface captured by the q parameter offsets some of the steepness and yields a 10 more gradual freezing curve, more similar to the actual experimental freezing probability 11 curve.

12 Two droplet freezing probability fits (dotted lines) are also plotted in Fig. 1 under 13 different environmental conditions. Instead of prescribing a cooling rate the freezing 14 probabilities are generated by running Eq. (7) for the entire temperature range with each 15 fit for $\Delta t = 1$ hour. One fit uses the same g distribution used previously, while the 16 additional single θ fit is approximated as a normal distribution with a near zero standard 17 deviation, similar to a Delta Dirac function. The resultant freezing probabilities are then 18 computed and plotted for every T. It can be seen that the g fit retains much stronger time 19 dependence, with the freezing probability curve shifting about 5 K warmer and the single 20 θ curve shifting just 1 K warmer for the 1 hour hold time.

21 This numerical exercise shows that wider g distributions yield stronger time 22 dependence due to the partial offset of the strong temperature dependence that the 23 nucleation rate in Eq. (2) exhibits. The result emphasizes that how the active sites are 24 modeled has consequences on what physical parameters (e.g. time, temperature, cooling 25 rate) can influence the freezing outcome and observed droplet freezing temperature 26 spectrum (Broadley et al., 2012). In Fig. 1 a wider q distribution resulted in higher 27 sensitivity to time, which resulted in a shift of the freezing curve to higher temperatures 28 as the system was allowed to temporally evolve at a fixed temperature. This significant 29 change in the freezing probability's sensitivity to temperature is the cause of the more 30 gradual rise in the freezing probability for the system when applying a non-Delta Dirac g 1 distribution. This is effectively enhancing the stochastic element in the particle's ice 2 nucleation properties. The shallower response of freezing probability to decreasing 3 temperature (deterministic freezing) creates a greater opportunity for time-dependent 4 (stochastic freezing) to manifest, as a larger fraction of the droplets spend more time 5 unfrozen. The enhancement of the stochastic element brings about a more important role 6 for time as shown in Fig. 1. The finding of this exercise is consistent with previously 7 published work on time dependent freezing such as those reported by Barahona (2012), 8 Vali and Stransbury (1966), Vali, (1994b), and Wright and Petters (2013), amongst 9 others.

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11 **3.2** Defining *g* as a normal distribution of ice nucleation activity

12 The fit for a particle-freezing curve such as the one considered in the previous section 13 (Fig. 1) does not have a unique solution. There are, mathematically speaking, infinite 14 solutions for the q distributions that produce a representative freezing curve. In any 15 considered distribution an ascending tail with increasing contact angle represents a 16 competition between more active but less frequent surface sites, and less active but more 17 frequent sites. Sites with lower activity and lower frequency have essentially zero chance 18 of contributing to the overall freezing probability, primarily due to the nucleation rate's, 19 J, exponential dependence on the energy barrier to nucleation and the freezing 20 probability's exponential dependence on J as shown in Eqs. (2) and (7). It is therefore 21 sufficient to conceptualize that the particle has a well-defined monotonic spectrum of 22 active sites increasing in frequency while decreasing in strength. The spectrum is 23 modeled as a continuum of ice nucleation activity described by the q distribution, as 24 depicted on the upper right hand corner in Fig. 2. Figure 2 also shows part of the g 25 distribution (the ascending part representing the monotonic spectrum of active sites) 26 retrieved for the case example in section 3.1 (log scale) discretized into numerical bins, 27 where the height of each bin represents the abundance of that θ across the particle's 28 surface. The area in each column thus represents the total surface area with that value of 29 θ . As in Fig. 2's inset the darker colors are used to emphasize more active ice nucleating 30 activity at the smaller contact angles.

1 The ascending part of the curve of the normal g distribution covering the smallest 2 (most active) values of θ in Fig. 2 can therefore capture this active site model. The wider 3 the defined g distribution (i.e. for a larger standard deviation, σ) the more diverse the 4 considered system is in its internal variability of ice nucleation activity. Since the 5 freezing probability is determined solely by a fraction of the ascent of the normal 6 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 7 8 made:

9
$$P_f = 1 - \exp\left(-\frac{A}{\dot{T}}\int_{T_i}^{T_f}\int_{0}^{\pi}J(T,\theta)g(\theta)d\theta dT\right)$$

10
$$\approx 1 - \exp\left(-\frac{A}{\dot{T}}\int_{T_i}^{T_f}\int_{\theta_{c_1}}^{\theta_{c_2}}J(T,\theta)g(\theta)d\theta dT\right)$$
 (10)

11 where θ_{c_1} and θ_{c_2} are the approximate cutoff points in the *g* distribution that contain the 12 critical range of the most active contact angles. Outside $[\theta_{c_1}, \theta_{c_2}]$ the less active contact 13 angles have a negligible contribution to the actual manifested freezing rate and freezing 14 probability. The critical contact angle range is a strong function of the area of the particle.

15 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 16 3(a) illustrates the process of identifying θ_{c2} . The blue curves represent freezing 17 probabilities computed via integrating Eq. (10) from 0 to a variable θ_{c2} . The red curve is 18 the freezing probability computed from integrating across the full θ range. As θ_{c2} is 19 20 increased the resultant curve (blue) approaches the curve computed from the full θ range 21 (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 22 range of θ . 23

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:

1
$$A_{nucleation} = A \int_{\theta_{c_1}}^{\theta_{c_2}} g(\theta) d\theta \qquad (11)$$

2 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 3 and $\theta_{c2} \approx 0.79$ rad. Application of Eq. (11) yields a total ice active surface area estimate 4 5 of 27 nm². Classical nucleation theory estimates that the area of a single active site is 6 6 nm² (Lüönd et al., 2010; Marcolli et al., 2007). The estimated total area of nucleation is 7 therefore consistent with this value and supports the argument that competition between 8 sites along the critical range of θ is taking place. However, the surface area where ice 9 nucleation is occurring remains a very tiny fraction of the total particle surface. This 10 further justifies the use of a continuum of surface area to define g as $dA/d\theta$ (Eq. 6). The 11 nucleating area is a function of both the g Gaussian distribution of θ , and the total 12 surface area of the considered particle. Figure 3(b) shows the g distribution in log scale 13 and highlights in red the fraction of the distribution covered by the critical contact angle 14 range.

15

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

18 Many droplet freezing array experimental methods such as those described in 19 Broadley et al. (2012), Murray et al. (2011), Vali (2014), Wright & Petters (2013), and 20 Hiranuma et al. (Hiranuma et al., 2015a) use atmospherically relevant particle sizes 21 (hundreds of nanometers to a few microns in diameter) but create the droplet array from a 22 prepared suspension of the particles of interest in water. The resultant particle 23 concentrations are typically high and the number of particles present in each droplet has 24 to be approximated using statistical methods. When total particle surface area is high 25 enough we hypothesize that it is conceivable that a threshold is reached whereby most of 26 the species' maximum possible external variability is already available within the 27 particle-droplet system. At this point it is approximated that no additional diversity in 28 external variability (ice active site ability or θ) is created by further increasing the total 29 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:

11
$$F = P_f(one \text{ system}) = 1 - \prod_{i=1}^n P_{uf,i}$$
 (12)

12 where *F* is the droplet frozen fraction, *n* is the number of particles per droplet, and $P_{uf,i}$ is 13 the probability that the particle *i* does not freeze. Further expanding the expression yields:

14
$$F = 1 - \exp\left[-t\left(\sum_{i=1}^{n} A_i \int_{0}^{\pi} J(\theta)g_i(\theta)d\theta\right)\right] = 1 - \exp\left[-t\int_{0}^{\pi} J(\theta)\sum_{i=1}^{n} (A_ig_i)d\theta\right]$$
(13)

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

16
$$\bar{g} = \frac{\sum_{i=1}^{n} (A_i g_i)}{A_t}$$
 (14)

17 where A_t is the sum of all particle surface area available inside a given droplet, and A_i is 18 the surface area representing that value of g_i (which is a function of θ). Equation (13) 19 then becomes:

20
$$\Rightarrow F = 1 - \exp\left(-tA_t \int_0^{\pi} J(\theta)\overline{g(\theta)}d\theta\right)$$
(15)

21 \bar{g} is the arithmetic average of all the *g* distributions for ensemble of particles in the 22 droplet (each particle has its own *g* distribution) with a cumulative area larger than the 23 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.

6 Above a certain surface area threshold it is conceptualized that the chance of an ice-7 nucleating particle surface not possessing the entire range of ice nucleating activity (θ) 8 becomes very small. The model therefore assumes that any particle or ensemble of 9 particles having a total surface area larger than the critical area can be approximated as 10 having \bar{q} describe the actual q distribution of the individual particles. In other words, for 11 large particles with more surface area than the critical area threshold, it is assumed that 12 the external variability between individual particles will be very small such that the 13 particle population can just be described by one average continuous distribution of the ice 14 active site ability, \overline{g} .

15 To resolve the active site distributions of the systems possessing particle surface areas 16 smaller than the critical area the first step is to approximate the critical area. Experiments 17 must start at very high particle surface area concentrations to ensure the number of 18 particles and total surface area per droplet exceeds the critical area. For the illite mineral 19 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} cm². The particle 20 21 number or surface area concentration is then decreased until the retrieved q distribution 22 (from the measured droplet freezing temperature spectrum for an array of droplets 23 containing particles) can no longer be reasonably predicted by \bar{q} . This point can identify 24 the parameter A_c , the critical area of the species under study. A schematic of the 25 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 μ m droplets were used and cooled at a cooling rate of 5 K/min. The curves from the highest particle concentration experiments, 7.42x10⁻⁶ cm² (6b) and 2.02x10⁻⁶ cm² (6a), are used to approximate the critical area of the system by first fitting the 6b curve with a *g* 1 distribution and then successfully predicting the 6a curve with the same q distribution 2 obtained from 6b and applying a particle surface area correction. The fit to the 6b curve is 3 done using Eq. (9) and follows the same procedure of least square error fitting described 4 in section 3.1. This g distribution is therefore assumed to be the \overline{g} of the considered 5 system with $\mu = 1.72$, and $\sigma = 0.122$. Note that above the threshold concentration A_c , approximated here as occurring around 7.42×10^{-6} cm², a change in the total available 6 7 surface area A is all that is required to account for how the change in particle 8 concentration shifts the droplet freezing temperature curve. This is not the case when 9 total area is less than the critical area A_c , as discussed next.

Moving to the lower concentration freezing curves $(1.04 \times 10^{-6} \text{ cm}^2 - 5a; \text{ and } 7.11 \times 10^{-7}$ 10 $cm^2 - 4a$) the transition to below the critical area begins to be observed. The solid lines 11 12 attempt to predict the experimental data points using \bar{q} . Predicting experimental data points for the 1.04×10⁻⁶ cm² (5a) system with the same \bar{g} distribution captures the 50% 13 frozen fraction point but fails at accounting for the broadness on the two ends of the 14 15 temperature spectrum. 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 16 17 temperature range over which freezing is occurring nor the 50% frozen fraction point.

18 We investigated a similar trend when freezing droplets containing commerical 19 Snomax (York International), and MCC cellulose (Sigma-Aldrich) particles immersed in 20 oil in our in-house cold plate system, described by Polen et al. (2016). The relevant 21 system details are that particle containing water droplets of approximately 450-550 μ m in 22 diameter are immersed in squalane oil, analogous to the method of Wright et al. (2013), 23 and the droplets' freezing temperature is determined optically during a constant 1 K/min 24 cooling cycle. Figure 6 shows decreasing concentration freezing curves for droplets 25 containing Snomax particles. Snomax is a freeze-dried powder manufactured from non-26 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 27 28 attributed to large protein aggregates, and Snomax is often used as a proxy for 29 atmospheric biological INP (Wex et al., 2015). A similar approach was undertaken in 30 which \bar{q} was retrieved using the highest concentration freezing curve (solid blue line).

1 The surface area density is assumed to be $1 \text{ m}^2/\text{g}$ though it is recognized that given the 2 protein aggregate based ice nucleating mechanism of Snomax it is difficult to attribute a 3 surface area of nucleation to a mass of Snomax powder. However, a surface area value 4 needs to be assumed to retrieve the ice nucleating properties using the framework 5 presented here for the sake of comparing Snomax to the other systems. For an assumed critical area of 4×10^{-6} cm² (the surface area at 0.1 wt%) \bar{g} was found to have $\mu = 0.66$, 6 and $\sigma = 0.055$. Unlike the illite dataset considered first, only 50% of the freezing 7 8 behavior of the second highest concentration freezing curve is captured by a frozen 9 fraction retrieved from \bar{q} (solid red line). Further lowering the concentration produces a 10 similar trend previously observed for the droplets containing illite, with similar freezing 11 onsets at higher temperatures but significant divergence at lower temperatures (purple 12 and green points). The frozen fractions retrieved from \bar{q} for the 0.08 wt% and 0.07 wt% 13 Snomax droplets (not plotted, as they almost overlap with the solid red line) do not 14 capture any of the freezing behavior measured indicating a very sensitive dependence of 15 active site density on surface area. A notable difference from the droplets containing illite 16 is that there is significant weakening in ice nucleation ability as the concentration/surface 17 area of Snomax is reduced. A potential explanation for this effect in the context of the 18 framework presented here will be discussed in a following section.

19 The freezing curves from droplets containing MCC cellulose powder (Hiranuma et al., 20 2015b) are shown in Fig. 7. For the MCC cellulose freezing curves \bar{q} was found to have $\mu = 1.63$, and $\sigma = 0.12$, from the 0.1 wt% curve. The freezing curve retrieved from 21 22 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 23 predicted directly from \bar{q} . Assuming a surface area density of 1.44 g/m² (Hiranuma et al., 24 2015a) the critical area for MCC cellulose is estimated to be $\sim 9.4 \times 10^{-4}$ cm². MCC 25 26 cellulose appears to exhibit ice nucleating capabilities reasonably stronger than illite and 27 significantly weaker than Snomax, based on the observed freezing temperature spectra 28 and the \bar{q} values retrieved. \bar{q} for Snomax was 0.66 \pm 0.055, 1.72 \pm 0.122 for illite NX, as 29 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 $[0, \pi]$, and the value of the active site distribution g^* for the particle *i* being sampled for at θ_r is assigned the value of $\overline{g(\theta_r)}$:

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

8 The g^* distributions within this numerical model are given an asterisk to indicate that 9 they are discrete distributions.

10 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 11 12 for so the modeled freezing curves can predict the behavior of the experimental freezing 13 curves. The value of n_{draws} typically ranges from 9 to 65 for the systems analyzed here and 14 is therefore a relatively soft optimization parameter with small dynamic range. The 15 sampled q^* distributions are normalized with respect to the estimated total surface area 16 for the freezing curve being modeled before being used to compute the freezing 17 probability. The bottom part of Fig. 4 shows a schematic of how q^* is retrieved from \bar{q} 18 using $n_{draws.}$ With the sampled g^* distributions the freezing probability of each droplet is 19 calculated using Eq. (9) and the frozen fraction curve is computed from the arithmetic 20 average of the freezing probabilities:

21
$$F(below\ critical\ area) = \frac{1}{N} \sum_{i=1}^{N} P_{f_i}$$
(17)

22 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

1 are both captured with the model. After \bar{g} was obtained from the high concentration data 2 above the critical area threshold, the only parameter that had to be optimized to produce 3 these accurately predicted freezing curves was n_{draws} . The values of n_{draws} for the lower 4 concentration freezing curves for each of the systems investigated here are 21 (2.02×10^{-6}) cm²), 19 (1.04×10^{-6} cm²), and 11 (7.11×10^{-7} cm²) for the droplets containing illite; 65 5 (0.09 wt%), 48 (0.08 wt%), and 23 (0.07 wt%) for the droplets containing Snomax; and 6 7 21 (0.05 wt%), 11 (0.01 wt%), and 9 (0.001 wt%) for the droplets containing cellulose. It 8 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 9 retrieved distribution will produce a freezing curve equivalent to using \bar{g} . 10

11 Perhaps the most notable characteristic is how the freezing curves of all three systems 12 analyzed ascend together early as temperature is decreased but then diverge as the 13 temperature decreases further (Figs. 5, 6a, and 7a). The closeness of the data at warmer 14 temperatures (the ascent) is interpreted by the framework as the presence of some rare 15 high activity active sites within the particle population under all the particle 16 concentrations explored in these experiments. At lower temperatures it appears that there 17 is a wider diversity in the activity of droplets that did not contain these rare efficient 18 active sites, and thus there is significant spread in the freezing curve for T < 242 K. In the 19 context of the framework presented here this can be attributable to strong external 20 variability of the ice nucleating population, with very strong/active nucleators causing 21 similar freezing onsets for different particle concentrations at the warmer temperatures, 22 and a lack of strong nucleators explaining the less consistent freezing of the unfrozen 23 droplets at lower temperature. Thus it follows that there is a wider spread in the freezing 24 curves for these droplets, as their freezing temperature is highly sensitive to the presence 25 of moderately strong active sites. This expresses a greater diversity in external variability 26 - the active site density possessed by individual particles from the same particle source. 27 In a later section the claim of more external variability contributing to the broader curves 28 below the critical area threshold is supported with a closer look at the numerical results 29 from the model.

1 The droplets containing Snomax displayed an immediate shift in freezing behavior for 2 small changes in concentration (from 0.1 wt% to 0.09 wt%) whereby a small drop in 3 concentration and thus surface area resulted in a broader temperature range over which 4 freezing of the droplets occurred (Fig. 6a). In the context of the model presented here this 5 is due to the mode of the \bar{q} distribution occurring at a very small (and thus very active) 6 contact angle of 0.66. In this contact angle range the barrier to nucleation is greatly 7 reduced causing freezing to be even more sensitive to the strongest active sites, and less 8 sensitive to the competing active sites that are weaker but more abundant (depicted in 9 Fig. 2), and therefore causing freezing curves to be quite steep versus T. A small change 10 in the surface area of this material may have produced a significant reduction in the 11 probability of droplets possessing these very strong nucleators, resulting in the observed 12 broadening of the freezing curves. This trend in Snomax is further investigated in a 13 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:

$$F = 1 - \exp(-n_s(T)A) \tag{18}$$

18 Equation (18) is similar in mathematical form to Eq. (15) and inherently assumes that 19 active site density can be defined as uniform over a particle's surface and is therefore 20 independent of the total surface area (it is multiplied by total surface area to estimate total 21 heterogeneous ice nucleation activity). From this point onwards n_s is regarded as the 22 deterministic analog of \bar{q} , where any time-dependent (stochastic) freezing is omitted. The 23 justification presented for the definition and use of the critical area quantity also applies 24 to the n_s framework, where it is argued that n_s ceases to become a proper representation of 25 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

1 both the red and blue curves were obtained from systems we have determined were above 2 the critical area threshold (Fig. 4). Further reduction of total surface area to below the 3 critical area threshold shifts the n_s values noticeably, as seen by the significant increase in 4 $n_{\rm s}(T)$ for the green curve. As all three curves were obtained by just varying the particle 5 concentration of the same species the same n_s values should be retrieved for all three 6 curves; the n_s scheme is designed to normalize for the total surface area or particle mass 7 present. This is successful for the higher particle surface area systems (red and blue 8 curves are similar) but not at lower particle area (green curve diverges). The large 9 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 10 11 with particle concentration or surface area. Further analysis will show this is not due to an 12 enhancement of ice nucleating activity per surface area but is actually a product of 13 external variability causing a broadening of the ice nucleating spectrum within the droplet 14 ensemble when total surface area is below the critical area threshold.

15 We have observed other similarly large effects of particle concentration on the 16 measured droplet freezing temperature spectrum and the retrieved n_s curves from our own 17 cold plate measurements. Figures 6b and 7b display n_m (active site density per unit mass 18 (Wex et al., 2015)) and n_s curves versus temperature for freezing droplets containing 19 Snomax and MCC cellulose, respectively. Similar to the data in Fig. 4b, these two 20 systems also exhibit a divergance in n_s (or n_m) as concentration (or surface area) is 21 decreased. Droplets containing MCC cellulose exhibited a much stronger sensitivity to 22 decreasing surface area than the droplets containing illite did, with changes in the values 23 of n_s of up to four orders of magnitude. The droplets containing Snomax on the other 24 hand were less sensitive to changes in surface area and exhibited an opposite trend in n_m , 25 with the values of n_m decreasing with decreasing concentration. This is consistent with 26 the analysis of the Snomax freezing curves, where the ice nucleating activity experienced 27 a substantial drop with decreasing surface area. It is further argued in a later section that 28 this is due to the very sharp active site density function g that Snomax particles appaear 29 to possess, resulting in steep droplet freezing temperature curves.

1 In assessing the three systems investigated here, it appears that the critical area 2 threshold depends a lot on the strength $(\overline{q(\theta)})$ of the ice nucleating activity for that 3 system. Capturing the critical area transition for illite required probing droplets that were 4 an order of magnitude smaller than the droplets containing Snomax and cellulose, 5 indicating a very large difference in the scale of the critical area. One explanation for this 6 behavior is that when ice nucleating activity is weak, nucleation can occur over a larger 7 total nucleating surface area. This means there is a smaller chance of losing critical active 8 sites in a droplet as the amount of material is reduced with decreasing particle 9 concentration. This argument is supported by these three data sets that span almost the 10 entire heterogeneous ice nucleation temperature range.

11 For the illite mineral suspensions Broadley et al. (2012) identified two total surface 12 area regimes by analyzing their droplet freezing curves. In the lower surface area regime 13 they observed a different freezing dependence on particle surface area than at higher 14 surface areas. At higher surface areas they saw no dependence of the freezing curves on 15 total particle surface area, which is inconsistent with both the stochastic and deterministic 16 frameworks. For larger droplets the transition seemed to occur at higher total particle 17 surface area indicating that there might be a particle concentration effect impacting the 18 total particle surface area per droplet. We have conducted our own illite measurements to 19 investigate this high concentration regime and further probe the applicability of \bar{g} to 20 freezing curves above the identified critical area threshold. Figure 8 shows the frozen 21 fractions versus temperature for an ensemble of droplets containing illite NX on our cold 22 plate system. The concentrations used were 0.5 wt%, 0.3 wt, 0.25 wt%, 0.2 wt%, 0.1 23 wt%, 0.05 wt%, 0.03 wt%, 0.01 wt%, and 0.001 wt% and the droplets were cooled at a 24 rate of 1 K/min. Average surface area estimates are made by assuming 500 μ m diameter 25 droplets and a surface area density of 104 m^2/g (Broadley et al., 2012). The solid lines are 26 applications of Eq. (15) with the same \bar{q} as the one found for the illite data set considered 27 above. It can be seen that this \bar{g} retrieved from cold plate experiments where droplets are 28 on the order of 10-20 μ m produces reasonable predictions of the freezing curves where 29 droplets are on the order of 500 μ m and thus contain particle surface areas up to five 30 orders of magnitudes larger. Another important conclusion that can be drawn from this

1 dataset is that high concentration data (0.25 wt%, 0.3 wt%, and 0.5 wt%) exhibited a 2 similar plateauing in freezing temperatures despite additional amounts of illite. This is 3 similar to the concentration range where Broadley et al. (2012) found a saturation effect 4 when further increasing the concentration of illite (over 0.15 wt%). This supports the 5 hypothesis that the high surface area regime for illite experiments is actually experiencing 6 a particle mass concentration effect and not a total surface area effect. The fact that the 7 concentration where this saturation effect is so similar while the droplet volumes and 8 consequently the amount of illite present between the two systems is quite different 9 points to a physical explanation such as particle settling or coagulation due to the very 10 high occupancy of illite in the water volume. These physical processes could reduce the 11 available particle surface area in the droplet for ice nucleation. Additionally, the high 12 concentration freezing curves show a good degree of broadening in the temperature range 13 over which freezing occurs. These three curves share a close 50% frozen fraction 14 temperature (with the 0.5 wt% oddly exhibiting a slightly lower 50% frozen fraction 15 temperature than the other two). One explanation that is consistent with the hypothesis of 16 particle settling and coagulation is that it becomes less likely that the droplets contain 17 similar amounts of suspended material when they are generated from such a concentrated 18 suspension (Emersic et al., 2015). This results in larger discrepancies in available surface 19 area between the droplets and therefore a broader temperature range over which the 20 droplets are observed to freeze.

21

22 **3.4** Comparison between \overline{g} , n_s , and other existing parameterizations of 23 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.

3 Fitting freezing curves with droplets below the critical area threshold with n_s yields 4 errors similar to fitting the curves with \bar{q} . Doing so has an inherent assumption of the ice 5 nucleation activity being totally internally variable. This is clear in comparing Eqs. (15) 6 and (18). That is \bar{g} and n_s both offer incomplete information about the distribution of ice 7 nucleation activity for a species. A similar conclusion along these lines was reached by 8 Broadley et al. (2012) when the authors noted that the best fits to their freezing curves 9 were achieved when the system was assumed to be totally externally variable. That is 10 when each particle was assumed to have a single contact angle but a distribution assigned 11 a spectrum of contact angles for each particle in the population.

12 There are other formulations that hypothesize an active site based or multi-component 13 stochastic model such as the ones described in Vali & Stransbury (1966), Niedermeier et 14 al. (2011), Wheeler and Bertram (2012), and Wright and Petters (2013). Vali and 15 Stransbury (1966) were the first to recognize that ice nucleating surfaces are diverse and 16 stochastic and thus active sites need to be assigned both a characteristic freezing 17 temperature as well as fluctuations around that temperature. Niedermerier et al. (2011) 18 proposed the soccer ball model, in which a surface is partitioned into discrete active sites 19 with each site conforming to classical nucleating theory. Marcolli et al. (2007) found a 20 Gaussian distribution of contact angles could best describe their heterogeneous ice 21 nucleation data in a completely deterministic framework. Welti et al. (2012) introduced 22 the alpha-PDF model where a probability density function prescribes the distribution of 23 contact angles that a particle population possesses, such that each particle is characterized 24 by a single contact angle. Wright and Petters (2013) hypothesized the existence of a 25 Gaussian probability density function for a specific species, which in essence is similar to 26 the \bar{q} framework described here. The notable difference is that their probability density 27 function was retrieved via optimizing for all freezing curves, and not from independently 28 fitting high concentration freezing curves as we have done here.

29 The n_s scheme is now more commonly used to describe and compare cold plate and 30 other experimental ice nucleation data instead of the multi-component stochastic schemes

1 (Hiranuma et al., 2015a; Hoose and Möhler, 2012; Murray et al., 2012; Wex et al., 2015). 2 This is in part due to the necessary inclusion of more variables required by other 3 frameworks (such as prescribing a discrete number of active sites in the soccer ball model 4 by Niedermeier et al. (2011)) than the simpler purely deterministic scheme of n_s . The new 5 formulation described here requires only prescribing a species' heterogeneous ice 6 nucleation ability as a function \bar{g} along with finding the critical area, A_c . The critical area 7 is determined by repeatedly measuring freezing curves for the same system or sample 8 using different particle concentrations. Varying particle concentration is already routinely 9 used in cold plate experiments to widen the droplet freezing temperature range that can 10 be measured. An estimate of the total surface area of the particles under study must be 11 made and associated with the retrieved freezing curves. While a process of random 12 sampling using n_{draws} is initially necessary to predict the freezing curves at more 13 atmospherically realistic concentrations below the critical area, in a following section we 14 will introduce easy to apply parameterizations that derive from this sub-sampling of 15 droplet freezing temperature spectra obtain above the critical area threshold.

16

17 **3.5** Dependence of g on ice nucleating particle size

18 The particle size dependence of the freezing probability comes from the exponential 19 dependence of the freezing probability on the surface area A as shown in Eq. (7). The 20 freezing probability's sensitivity to surface area is the same as its sensitivity to time 21 however the quadratic dependence of area on radius makes size a more sensitive 22 parameter than time. Furthermore, there might be more subtle size dependencies in the q23 function itself. For a given particle type, whether size affects the diversity (internal 24 variability) of nucleating sites is not something that can be trivially probed 25 experimentally. To accurately test any potential size dependence, particles of varying 26 sizes need to be probed individually and compared. Measurements in which particles 27 were size selected before assessing their ice nucleation ability have been performed, such 28 as those using continuous flow diffusion chambers as described in Koehler et al. (2010), 29 Lüönd et al. (2010), Sullivan et al. (2010a), Welti et al. (2009), among others. However, a 30 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.

4 The argument for the existence of a species' specific critical area can be made for 5 either a total number of particles in a specific size range or a total particle surface area. 6 Assuming that a single species' surface area does not undergo intensive changes in its ice 7 nucleation properties (such as chemical processing as discussed in Sullivan et al. (2010a, 8 2010b)) a cut-off critical size can be defined. Above this critical size the active site 9 distribution is \bar{g} while below it is some distribution of g's that can be sampled from \bar{g} . In 10 one of the cases studied here in Fig. 5 for illite mineral particles the critical surface area was around 10⁻⁶ cm². This corresponds to a single spherical particle with an equivalent 11 diameter of around 10 µm, a size cutoff that is quite atmospherically relevant (DeMott et 12 13 al., 2010). The vast majority of the atmospheric particle number and surface area 14 distributions are found at sizes smaller than 10 µm. Thus we conclude that for illite 15 mineral particles, individual atmospheric particles will not contain the entire range of ice 16 active site activity (\bar{q}) within that one particle, and each particle's ice nucleation ability is 17 best described by an individual g distribution (that is a sub-sample of \overline{g}).

Application of Eq. (11) to find $A_{nucleation}$ for illite systems 6a (2.02×10⁻⁶ cm²) and 5a 18 $(1.04 \times 10^{-6} \text{ cm}^2)$ from Broadley et al. (2012) gives insight into how the nucleating area is 19 20 influencing the shape of the freezing curves. System 6a is where the critical area cutoff 21 was found to occur while 5a started to exhibit the behavior of a broader freezing curve 22 with a similar onset of freezing but with a diverging tail, indicating it is below the critical 23 surface area. In Fig. 6 the average cumulative ice nucleating area computed from Eq. (11) 24 is plotted against the critical contact angle range for the two systems. The total nucleating 25 area at low contact angles is strikingly close between the two systems. This is because 26 statistically the chance of possessing rare and highly active sites in an ensemble as large 27 as system 5a is high as these occupy a small portion of the total particle area but have a 28 substantial impact on the freezing behavior. This explains why the onset of freezing for 29 the two curves is so similar. The diverging tail can be attributed to the divergence of the 30 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.

5 A similar nucleating area analysis was performed on the droplets containing Snomax 6 and is shown in Fig. 12. The cumulative nucleating areas for the droplets with Snomax 7 concentrations of 0.09 wt% and 0.08 wt% (red and green data in Fig. 8, respectively) are 8 calculated and shown over the critical contact angle range with the same color scheme. 9 Unlike the illite system, droplets containing Snomax exhibit a more straightforward trend 10 in cumulative nucleating area vs. critical contact angle. The cumulative nucleating area is 11 consistently smaller in the 0.08 wt% system compared to the 0.09 wt% experiment, 12 indicating that as the particle surface area is reduced the strong nucleators are reduced 13 uniformly over the critical contact angle range. This supports the idea that the range of 14 active site activity is much smaller for this very ice active system. We propose that this is 15 what explains the decrease in n_m with decreasing concentration observed in Fig. 5.

16 The implications of this analysis on the size dependence of g is that below the critical 17 surface area particles may or may not possess freezing behavior similar to the particles 18 above the critical area threshold. The broadening of the freezing curves in the systems 19 analyzed here as the surface area is reduced is interpreted as heterogeneity in ice 20 nucleating ability between the different particles (external variability) and not due to the 21 internal variability within the individual particles themselves. While the broadness of the 22 curves above the critical surface area can be attributed to internal variability, the 23 additional broadness in curves below the critical area cutoff are a result of external 24 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-

1 dimensional variability may be necessary, such as a series of g or \overline{g} distributions. For 2 illite it seems that external variability is dominant and thus one active site distribution or 3 n_s parameterization does not properly represent the species' ice nucleation behavior. The 4 critical area effect is even more substantial for cellulose and Snomax as their ice 5 nucleating activity is much stronger than illite. However, if a system's global 6 \bar{q} distribution is obtained then its full ice nucleation behavior is contained within and can 7 be successfully subsampled from \bar{q} . Cold plate droplet freezing measurements thus 8 remain a crucial tool for unraveling the complex behavior of ice nucleating particles, 9 particularly when a large particle concentration range is probed.

10 Cold plate experimental data potentially provides sufficient information to describe heterogeneous ice nucleation properties in cloud parcel and atmospheric models, however 11 12 the analysis undertaken here suggests that retrieving one active site density 13 parameterization (e.g. n_s) and applying it to all surface areas can result in misrepresenting 14 the freezing behavior. When samples are investigated, probing a wide concentration 15 range enables the determination of both general active site density functions (e.g. \bar{q}) as 16 well as the behavior of the species' under study at concentrations below the critical area 17 threshold. Once this analysis is undertaken more comprehensive parameterizations can be 18 retrieved as will be developed in the next section.

19 The critical area analysis carried out in this paper emphasizes the dangers in 20 extrapolating the freezing behavior of droplets containing a large concentration of 21 particle to droplets containing smaller concentrations or just individual particles. 22 Applying a parameterization such as n_s directly to systems below the critical area 23 threshold in a cloud parcel model for example yields large differences in the predictions 24 of the freezing outcome of the droplet population. As the concentration of the species 25 within the droplets was decreased in the cold plate freezing spectra considered here the 26 actual freezing temperature curves diverged more and more from those predicted when 27 the systems were assumed to be above the critical area. This led to significant changes in 28 the retrieved n_s values, as shown in Figs. 4, 6b, and 7b. The large effects of concentration 29 on the droplet freezing temperature can be directly observed in the frozen fraction curves 30 plotted in Figs. 5, 6a, and 7a. Differences between observed frozen fraction curves and 1 ones that assumed uniform active site density yielded errors in the temperature range the 2 droplets froze over as well as the median droplet freezing temperature. Therefore, a cloud 3 parcel model would be unable to accurately predict the freezing onset or the temperature 4 range over which freezing occurs using a single n_s curve obtained from high 5 concentration data. This has important consequences for the accurate simulation of the 6 microphysical evolution of the cloud system under study such as the initiation of the 7 Wegener-Bergeron-Findeisen and the consequent glaciation and precipitation rates 8 (Ervens and Feingold, 2012; Ervens et al., 2011).

9 Figure 13 shows the range of n_s values for illite NX mineral compiled from seventeen 10 measurements methods used by different research groups, the details of which are 11 described by Hiranuma et al. (2014). The range of data is summarized into shaded 12 sections to separate suspended droplet freezing techniques (such as a cold plate) from 13 techniques where the material under investigation is aerosolized before its immersion 14 freezing properties are assessed (such as the CFDC or AIDA cloud expansion chamber). 15 The aerosol techniques tend to produce higher retrieved n_s values than those obtained by 16 the wet suspension methods. $n_{\rm e}$ data spanning a surface area range of about five orders of 17 magnitude retrieved exclusively from both our cold plate measurements and Broadley et 18 al. (2012) measurements are also plotted. Data presented in Fig. 8 that was consistent 19 with a \bar{g} treatment is plotted as n_s (gold and green rectangles). These two datasets along 20 with what was identified as the critical area dataset from the Broadley et al. experiments 21 follow a consistent n_s line that lies within the range of the suspended droplet techniques. 22 The blue triangles are low surface area data points retrieved from dataset 4a from the 23 Broadley et al. measurements. As was argued earlier, this system exhibits higher n_s 24 values, an artifact of the increased active site density of some of the particles. While this 25 data is retrieved with a cold plate, it falls within the range of the aerosolized methods 26 where particle surface areas are small. Finally, more of the suspension method range of 27 retrieved n_s can be spanned by data where the concentration saturation effect takes place. 28 Data that exhibited this behavior from the CMU cold plate system (purple hexagons) and 29 the Broadley et al. system (red and brown bowties) are plotted. This effect tends to 30 underestimate n_s since additional material is added while the freezing behavior remains 31 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.

5 Various research groups using wet suspension methods typically vary particle 6 concentrations to span a wider range of measureable droplet freezing temperature 7 (Broadley et al., 2012; Murray et al., 2012; Wright and Petters, 2013). Our analysis 8 indicates that by doing so different n_s values are in fact retrieved, just due to changes in 9 concentration. This highlights the importance of obtaining n_s values that overlap in 10 temperature space, to evaluate if n_s is in fact consistent as concentration is changed. We 11 therefore provide the critical area framework presented here whereby ice nucleating 12 surface area dependence is more complex than depicted in traditional deterministic and 13 stochastic models, as a potential source of the discrepancy in n_s values for the various 14 measurement techniques. This commonly observed discrepancy in n_s between droplet 15 suspension and aerosol INP measurement methods is the subject of ongoing 16 investigations, such as the INUIT project that is currently focusing on cellulose particles, 17 a system we have included here. As the results from this multi-investigator project have 18 not yet been published we cannot present them here. They show a similar trend as for the 19 illite NX data, where the aerosol methods retrieve higher n_s values than the droplet 20 suspension methods do. By changing particle in droplet concentration we can span much 21 of the difference in n_s between the two groups of methods, as was shown for the illite NX 22 measurements.

23 **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:

3
$$F = 1 - \exp\left(-tA\int_{0}^{\pi} J(\theta, T)\overline{g(\theta)}d\theta\right)$$
(15)

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

6
$$F = 1 - \exp\left(-tA_c \int_{0}^{\pi} \left(J(\theta, T)\overline{g(\theta)}d\theta\right)h(A, T)\right)$$
(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 $h(A_c, T) = 1$.

10 An example of retrieving values of h(A, T) would be in correcting the solid line for 11 system 4a (7.11×10⁻⁶ cm²) to the dotted line in Fig. 5. The solid line is the basic use of 12 Eq. (15) however it was shown that the considered experimentally retrieved freezing 13 spectrum was below the critical area threshold. By taking the ratio of the dotted and solid 14 lines values of *h* can be retrieved for that surface area at each temperature point.

15 If the aerosol particle population is polydisperse and its size distribution can be 16 expressed as a function of surface area, the frozen fraction can be written as:

17
$$F = \int_{A_i}^{A_f} \left[1 - \exp\left(-tA \int_0^{\pi} (J(\theta, T)\overline{g(\theta)}d\theta)h(A, T)dA\right) \right]$$
(20)

18 where A_i and A_f are the minimum and maximum values of the surface areas of the 19 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), 1 and (20) can be applied with a \bar{g} distribution that is the surface area weighted average of 2 the \bar{g} distributions of all the considered species. This can be expressed as:

6
$$\bar{g}_{average} = \frac{1}{A} \sum_{i=1}^{m} A_i \bar{g}_i$$
(21)

3 where A_i is the surface area of the species i, \bar{g}_i is the \bar{g} distribution of the species i, and m4 is the total number of species. If the system is externally mixed, the frozen fraction can be 5 expressed as:

7
$$F = \frac{1}{m} \sum_{i=1}^{m} F_i$$
 (22)

8 where F_i is the frozen fraction of droplets containing particles of species *i* and can be 9 retrieved from Eq. (19) or (20).

10

11 **5 Conclusions**

12 Cold plate droplet freezing spectra were carefully examined to investigate a surface 13 area dependence of ice nucleation ability whereby one active site density function such as 14 $n_{\rm s}$ cannot be extrapolated from high particle surface area to low particle surface area 15 conditions. A method based on the notion of a critical surface area threshold was 16 presented. It is argued that a species' entire ice nucleating spectrum can be confined 17 within a global probability density function \bar{q} . For a system, be it one particle or an 18 ensemble of particles, to have a total surface area greater than the critical area is a 19 question of whether the surface is large enough to express all the variability in that 20 particle species' ice active surface site ability. By analyzing droplets containing illite 21 minerals, MCC cellulose, and commercial Snomax bacterial particles, it was shown that 22 freezing curves above a certain critical surface area threshold could be predicted directly 23 from the global \bar{q} distribution obtained from the high particle concentration data alone. 24 The lower particle concentration freezing curves were accurately predicted by randomly 25 sampling active site abilities (θ) from \overline{g} and averaging their resultant freezing 26 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.

3 We found that the shifts to colder freezing temperatures caused by reducing the 4 particle concentration or total surface area present in droplets cannot be fully accounted 5 for by simply normalizing to the available surface area, as is done in the ice active site 6 density (n_s) analysis framework. When the surface area is below the critical area 7 threshold the retrieved values of n_s can increase significantly for the same particle species 8 when the particle concentration is decreased. Above the critical area threshold the same n_s 9 curves are retrieved when particle concentration is changed. Atmospheric cloud droplets 10 typically contain just one particle each. Therefore, this effect of particle concentration on 11 droplet freezing temperature spectra and the retrieved n_s values has important 12 implications for the extrapolation of cold plate droplet freezing measurements to describe 13 the ice nucleation properties of realistic atmospheric particles.

14 Systems that probe populations of droplets each containing one particle such as the 15 CFDC are unable to probe a large particles-in-droplet concentration range but are 16 powerful tools for the real-time investigations of ice nucleating particles at the realistic 17 individual particle level (DeMott et al., 2010; Sullivan et al., 2010a; Welti et al., 2009). 18 The frozen fraction curves produced from such an instrument do not provide enough 19 information to associate the observed variability in ice nucleation ability to internal or 20 external factors. However, future laboratory studies using the critical area-cold plate 21 technique we have introduced here (e.g. Fig. 4) will provide new insight into the critical 22 area thresholds of internal variability in ice active site ability for different species. This 23 will produce more informed assumptions regarding the variability in ice nucleation 24 properties observed through online field instruments, specifically when the measurements 25 are made in conjunction with single particle chemical analysis techniques (Creamean et 26 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

1 properties of particles in cloud and atmospheric models. However careful examination of

2 the surface area dependence of ice nucleating ability of a species allows more accurate

3 retrievals of active site density distributions that properly encompass this dependence.

4

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3 Figure 1. Experimentally determined freezing probabilities and fits from freezing of a 4 droplet containing a single large $\sim 300 \,\mu\text{m}$ diameter volcanic ash particle, from Fornea et 5 al. (2009). Red dots are experimental freezing probabilities retrieved from repeated 6 droplet freezing measurements. The red line is a fit to the data using classical nucleation 7 theory and the assumption of a single contact angle (θ). The blue line is a fit to the data 8 using the g framework developed here, which describes a Gaussian distribution of θ . The 9 g fit has a least square error sum of 0.0197, $\mu = 1.65$, and $\sigma = 0.135$. The dotted red line 10 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 11 12 multiple θ distribution described by g after the same temperature hold simulation.

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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 ($\mu = 1.65$, and $\sigma = 0.135$, 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).





4 Figure 3. Left (a): Identifying the critical contact angle range. The thin blue curves are 5 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 6 7 red curve is obtained from application of the complete Eq. (7), which integrates over the 8 full contact angle range. Both approaches use the same q distribution retrieved for the 9 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 10 angle range retrieved in Section 3.2 ($\theta_{c1} \approx 0.4$ rad and $\theta_{c2} \approx 0.79$) in red. 11



4 Figure 4. Top: Schematic summarizing the procedure for determining the critical area. 5 Left (a): The frozen fraction freezing curves shift to lower temperatures initially due 6 solely to the decrease in total surface area of the ice nucleating particles (curves 1 & 2). 7 As the total surface area of the particles is decreased below the critical area threshold 8 $(q \neq \overline{q})$ the slope of the freezing curve also broadens because the effective distribution 9 of ice nucleating sites has changed – more external variability has been introduced (curve 10 3). **Right (b):** Ice active site density (n_s) retrieved from the frozen fraction plots on the 11 left for the same three particle concentration systems. Above the critical area limit (g =12 \bar{g}) the two n_s curves are essentially the same, but below the critical area threshold ($g \neq a$ 13 \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{q} 14 15 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 16 each draw a random contact angle from the full range of contact angles $[0, \pi]$ is chosen 17 18 after which the value of q^* at that contact angle (right) is assigned the value of \bar{q} at the 19 same contact angle (left). 20





3 Figure 5. Experimental freezing curves for different surface area concentrations of illite 4 mineral powder immersed in 10-20 µm diameter water droplets taken from Broadley et 5 al. (2012) (circles). Lines are modeled predictions of the same data using the q^* 6 distribution method. Solid lines are produced directly from the global \bar{q} distribution first 7 obtained from the high concentration system. The dashed lines are obtained by randomly 8 sub-sampling the global \bar{q} distribution to obtain q^* and following a surface area 9 correction, as described in the text.

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17 Figure 6. Left (a): Experimental freezing curves for different mass concentrations of 18 commercial Snomax powder immersed in 200-300 um diameter water droplets obtained 19 using the CMU cold plate (circles). Solid lines are fits produced from randomly sampling 20 from the \bar{q} distribution retrieved from the highest concentration freezing curve (0.1 %wt). 21 Dashed lines are fits produced from randomly sampling from the \bar{q} distribution and a 22 surface area correction. The second highest concentration freezing curve (0.09 %wt) is 23 used to confirm the critical area threshold had been exceeded. Right (b): Ice active site 24 density (n_m) retrieved from the frozen fraction data on the left. A trend of decreasing n_m 25 with decreasing concentration is observed for the droplets containing Snomax.





4 Figure 7. Left (a): Experimental freezing curves for different mass concentrations of 5 MCC cellulose powder immersed in 500-600 µm diameter water droplets obtained using 6 the CMU cold plate (circles). Dashed lines are fits produced from randomly sampling 7 from the \bar{q} distribution retrieved from the highest concentration freezing curve (0.1 wt%, 8 blue solid line) and a surface area correction. The second highest concentration freezing 9 curve (0.05 wt%, red) is used to confirm the critical area threshold was exceeded. **Right** 10 (b): Ice active site density (n_s) retrieved from the frozen fraction data on the left. A trend 11 of increasing n_s with decreasing concentration is observed.

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Figure 8. Experimental freezing curves for different mass concentrations of illite NX powder immersed in 500-600 μ m 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.

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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).

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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).

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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).