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Interactive Comment

Interactive comment on "Heterogeneous ice nucleation: bridging stochastic and singular freezing behavior" *by* D. Niedermeier et al.

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First of all we would like to thank referee 3 for his constructive comments and suggestions. In the following the comments will be addressed and discussed.

General comments

There are two classical concepts of heterogeneous nucleation. The first one starts from consideration of the random motions of single water molecules, a sufficient number of which have to combine to form a stable ice germ: this is the concept of heterogeneous nucleation as a stochastic process. The second viewpoint starts from the observation that ice germs preferentially form at certain features on a nucleus, called active sites. As soon when the thermodynamic conditions (supercooling, supersaturation) al-

low the first (i.e. most appropriate) active site to stabilize a cluster of water molecules sufficiently, an ice germ forms. This is the so-called singular hypothesis. These two concepts are extreme in the following sense. The singular hypothesis assumes nucleus surfaces with a variety of features, i.e. the active sites, which may have widely varying nucleation thresholds. Ice germs can only form at the active sites and nowhere else. In contrast, the stochastic concept assumes a featureless surface where an ice germ can form everywhere with uniform probability. This is clearly a mathematical idealisation which could be approximated by a surface densely und uniformly packed with active sites of uniform nucleation properties. There are many measurements that do not actually fit into one of these extreme concepts, and therefore attempts have been undertaken to find concepts in between these two extremes. The authors of this paper have build such a bridge by essentially retaining the classical nucleation theory but with a non-uniform nucleus surface where the contact angle varies. This is an obvious generalisation and worth the trying. The paper should be published after consideration of the following points.

Section 2

On first reading this section was a bit difficult to understand and surprising. Looking at Figure 1 and without reading the text first I would have come to the conclusion that the green points represent singular behaviour while the orange and blue points represent stochastic behaviour. The reason for this misunderstanding was that the diagram shows nucleation as a function of supercooling. While the behaviour of "frozen Fraction" vs. time at constant temperature is intuitively understandable (that is some "radioactive decay" type behaviour vs. constant zero or constant 100 percent), the behaviour as function of supercooling is not easily intuitively clear. Certainly, it depends on the two timescales involved (the cooling timescale and the T-dependent nucleation timescale). The argumentation would become clearer when the authors provide in a first paragraph a brief introduction on what one should expect in a "frozen fraction" versus supercooling diagram for the two extreme scenarios. Finally, it is not clear to

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me what you mean with "measurement time". I believe, in your experiment you cool your ensemble of drops step by step (e.g. by one degree) and let it then rest for a while which is the "measurement time". This should be explained.

Considering the reviewer's concerns, we rewrote the paragraph to make the Figure clearer:

" First, Shaw et al. (2005) and Durant and Shaw (2005) measured the freezing temperature of a water drop containing a single mineral (volcanic ash) particle, exposed to a constant cooling rate (Fig. 1). By repeating the measurement tens or hundreds of times a distribution of freezing temperatures was obtained, corresponding directly to inherent randomness of the freezing process. This result, the appearance of random fluctuations in freezing temperature for an identical particle unambiguously contradicts the singular description, for which a single particle is characterized by a single, deterministic threshold freezing temperature. Second, Niedermeier et al. (2010) measured the freezing temperature of large numbers of water droplets each containing a size-selected, monodisperse mineral particle (Arizona Test Dust, ATD). They found that ATD nucleated ice over a broad temperature range and the determined freezing temperature distributions could be parameterized using either stochastic or singular descriptions. Subsequently, an attempt to distinguish experimentally between singular and stochastic behavior was made (not shown in Niedermeier et al. (2010)). Experiments were repeated under nearly identical thermodynamic conditions but with increased nucleation time (the time interval within which supercooled droplets can freeze), but the freezing behavior remained essentially unchanged (Fig. 1). This apparently contradicts the stochastic description, for which an increase in nucleation time should lead to an increase in the freezing probability."

Section 3

I find your model description unnecessarily long. You could simply say: "We consider a large number of droplets, each containing one single nucleus of identical surface

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area. On each nucleus surface we assume a fixed number nsite of active sites with a gaussian distribution of contact angles θ, cut off at 0 and π. The model contains three variables, namely n_{site}, and the mean value μ_θ and standard variation σ_θ of the distribution of contact angles." This is essential what you are saying and it fits in few lines. There are further features of your model that are not essential. These are: the spherical shape of the nuclei and the division of the nucleus surface into equally sized patches.

We think it is really important to describe the model setup step by step, also in light of reviewer 1 and 2's comments. In fact, after careful consideration, we have decided to make the explanation even more descriptive and hope the reviewer will accept our reasoning:

1. We consider a large number N_0 (statistical ensemble) of spherical 'ice nucleus' particles of identical size, each particle immersed in a water droplet. If the population of particle-containing water droplets is assumed to be exposed to uniform thermodynamic conditions, the fraction of frozen droplets at a given time and temperature can be directly related to the probability of freezing on a particle of the specified size, composition, etc.

2. The properties of individual particles are not necessarily identical, but are drawn from a probability distribution. To that end, the surface of each particle is imagined to be divided into a number n_{site} of surface sites, with each site having well-defined properties (e.g., interfacial free energy). The word site is used to denote a surface two-dimensional 'patch' of finite extent and the image of a spherical particle covered by a finite number of patches leads to the colloquial name 'soccer ball' model. For simplicity, n_{site} is identical on all particles and the sites are assumed to be of the same size, $s_{\text{site}} = S_{\text{p}}/n_{\text{site}}$, where S_{p} is the particle surface area. Hence each surface site is associated with a given area depending on the number of sites per particle. Since each individual site has homogeneous prop-

erties, ice embryo formation can occur randomly at some point on the given site or patch. In other words, ice formation on any given site can be considered to be described by classical nucleation theory.

3. Each surface site, i, is characterized by a fixed, but randomly chosen water contact angle θ_i. For simplicity, the contact angle distribution function $P(\theta)$ is assumed to be the integral over the Gaussian (error function) characterized through mean μ_θ and standard deviation σ_θ. The contact angle distribution is discretized in 1800 bins between 0 and π and through uniformly distributed random numbers $n \in [0,1]$ each site is associated with a specific contact angle, shown in the right panel of Fig. 2 through θ_i.

The latter are only needed because one needs their area for multiplication with the "per unit area" nucleation rate. The only important thing is that the nuclei contain active sites with a certain distribution of nucleation thresholds. It does not matter where these sites are and how they get their activities. I am also convinced that you might easily allow that different nuclei contain different numbers of sites (for instance a narrow Gaussian distribution) without changing your results significantly.

Of course we could vary the number sites/patches per particle too, however, in our opinion that would not in principle change the observed transition from stochastic to apparently singular behavior, i.e. the main message of this paper. We desire to keep the model as simple as possible and still allow stochastic-singular transition, so nothing was changed.

Case A: the population is completely uniform whenever $\sigma_\theta = 0$ independent of nsite.

Correct, we changed this: "(A) When $\sigma_\theta = 0$, the population is completely uniform."

Equation 1: Pfreeze does not depend on the contact angle itself. It depends instead on the mean contact angle and the standard deviation.

Correct, now $\theta_i = \theta_i(\mu_\theta, \sigma_\theta))$

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Conclusions

Your central conclusion is that one doesn't need active sites to explain singular behaviour. To me this sounds like an overinterpretation of your model, which has nuclei with patches of low contact angles instead of active sites. However, isn't such a low-? patch nothing than a convenient numerical representation of an active site? On real atmospheric or laboratory nuclei there are features like cracks, molecules with unsaturated bonds, etc. Therefore I suggest you rephrase your statement in a way like: Whether ice nuclei display singular or stochastic freezing behaviour is not a question of the presence or absence of active sites (they are present), it is a question of how many of them are present on the IN surface and how variable are their properties. Low variability leads to stochastic behaviour, large variability on each single IN leads to singular behaviour.

Due to this and other comments (e.g., by Gabor Vali) we modified the conclusion section to:

"Finally, the central insight gained from this work is: based on classical nucleation theory alone, a population of particles can exhibit behavior over a continuous range, from purely stochastic to nearly singular. The emergence of singular, or nearly singular behavior arises from the existence of sites possessing widely differing nucleation rates (or, in the language of classical nucleation theory, widely differing contact angles), with each individual site exhibiting purely stochastic behavior. Therefore, an idealized population of statistically similar but individually different particles, characterized by a relatively wide distribution of surface free energies, and subject to purely stochastic freezing behavior, can manifest what traditionally has been interpreted as singular behavior: weak time dependence of freezing probability, and wide freezing temperature distributions. Interpreted in this light, the 'lack of time dependence' typical of the singular behavior is only meaningful when the time scale of an experiment or measurement is defined. Fundamentally, in the conceptual model described here, the freezing process is stochastic, so there is always a time dependence. It just may be that the time dependence occurs with a characteristic time scale much less than or much greater than the time scales resolved in a hypothetical experiment. In this regard, the detailed implementation of the model (i.e., specific choice of Gaussian distribution for contact angles) is not so important as its essential elements: statistically similar particles covered by surface patches following a classical, stochastic nucleation behavior."

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