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Atmospheric Chemistry and Physics Discussions

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 2 for his valuable comments and suggestions. In the following the comments will be addressed and discussed.

This manuscript addresses a topic that is important for the treatment of heterogeneous ice nucleation, namely, whether this process should be described using a stochastic or a singular approach. The answer of the authors to this question is that ice nucleation is fundamentally a stochastic process but that for realistic atmospheric particle populations this process can be masked by the heterogeneity of surface properties. The authors present a "soccer ball" model that they use in idealized simulations to illustrate how the experimental conditions and the properties of the ice nuclei can lead to seemingly singular or stochastic behavior. This part of the paper is very convinc-

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ing. However, it remains unclear what the principle difference and advantage of this model is compared with the modified singular description and the models developed by Marcolli et al. (2007) and Lüönd et al. (2010).

Our conceptual model is fundamentally based on the stochastic view of nucleation: That is, nucleation is viewed as always occurring as a result of random fluctuations of water molecules leading, eventually, to a critical ice embryo able to grow spontaneously. In contrast, Vali and Stansbury (1966) stated that the ”[...] properties of the nucleating site determine the mean size of the embryo, as in the singular hypothesis, with the fluctuations about the mean size adding a stochastic element to the process of nucleation." (Page 494) This statement seems to imply that the nucleation is a mixture of the stochastic and singular behavior, but in fact it is still fully stochastic.

In our opinion, the main difference of our model compared to those of Marcolli et al. (2007) and Lüönd et al. (2010) is that allows for considering both an ensemble of IN with homogeneous surfaces (one contact angle per IN similar to the contact angle approach of Marcolli et al., 2007 and the alpha-pdf-model of Lüönd et al. (2010), and IN with varying number of active sites/patches (similar to active site approach of Marcolli et al., 2007 and Lüönd et al. (2010)) however with contact angles for the sites/patches being collected form a Gaussian distribution. It should be noted, that the models of Marcolli et al. (2007) and Lüönd et al. (2010) in principle could have been used to generate results similar to those presented in the present paper. The main intended contribution of this paper is in the exploration of the transition between singular and stochastic behavior. Our model was developed to be as simple as possible but to still allow the transition to be manifested in the variation of parameters with clear physical interpretation.

The following statements were added to or rewritten in the text:

"Various combinations of these two extremes have been postulated, originally by Vali and Stansbury (1966), and can be broadly regarded as falling within the “modified sin-

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gular hypothesis" (Vali, 1994; Marcolli et al., 2007; Vali, 2008; Lüönd et al., 2010). The experiments of Vali and Stansbury (1966) and Vali (1994, 2008) consisted of repeated freezing and melting cycles of water droplets containing different kinds of particles, and freezing temperatures with small fluctuations were observed. These findings were interpreted as reflecting the existence of characteristic freezing temperatures for active sites on the immersed particles, about which stochastic effects lead to slight variability in the freezing temperatures. The concept can be expressed as particles possessing active sites, each with a distribution of nucleation rates, and with nucleation rate being a steep function of temperature (see Comment by Gabor Vali[1] and Figure 1 within this comment)."

"The work extends the concept of Marcolli et al. (2007) and Lüönd et al. (2010), who found that their measurements were best described using the active site approach while keeping the stochastic concept of a nucleation rate. Our conceptual model, which is for convenience placed in the context of immersion freezing but could just as easily be adapted to deposition nucleation, is fundamentally based on the stochastic view of nucleation: That is, nucleation is viewed as always occurring as a result of random fluctuations of water molecules leading, eventually, to a critical ice embryo able to grow spontaneously."

"For $n_{\mathsf{site}} = 1$ the particle surface is completely homogeneous in its surface properties (one contact angle per IN similar to the contact angle approach of Marcolli et al. (2007) and the alpha-pdf-model of Lüönd et al. (2010)), i.e., the particle surface is featureless, and ice embryo formation can occur everywhere on the nucleus with uniform probability (purely stochastic view). With increasing number of patches or sites a) the size of each patch/site decreases (at least to the limiting size of an ice embryo) and b) the variety of surface properties between the patches/sites increases with broadening contact angle distribution (similar to active site approach of Marcolli et al. (2007) and Lüönd et al. (2010) however with contact angles for the sites/patches being collected

[1]http://www.atmos-chem-phys-discuss.net/11/C315/2011/acpd-11-C315-2011-supplement.pdf

form a Gaussian distribution and different site/patch size.)."

The "soccer ball" model and the model of Marcolli et al. (2007) and Lüönd et al. (2010) both assume that the surface of each particle can be divided into a number of surface sites with each site having well-defined properties. The nucleation rate on individual sites is described by Classical Nucleation Theory with contact angles that can vary between surface sites and consequently between particles, too. In both approaches, the contact angles are drawn from a contact angle distribution function. The main difference that I can find between the two approaches is, that the "soccer ball" model assumes that the whole surface of the particle is active as IN while the approaches by Marcolli et al. (2007) and Lüönd et al. (2010) limit IN activity to active sites. The authors should therefore more explicitly discuss the new features and the advantages of their "soccer ball" model. Having to divide the particle surface into an arbitrary number of patches with different surface properties might indeed become a disadvantage when the model is applied to polydisperse aerosols.

At the moment our model is purely conceptual and our intention has been to show that a purely stochastic model can produce singular behavior, and to explore the transition from one limit to the other. In this respect there is an advantage to allowing the entire particle to have completely homogeneous surface properties, thereby representing the purely stochastic limit. Whether the models of Marcolli et al. (2007) and Lüönd et al. (2010), or our model are more suitable for interpreting and parameterizing experimental data, in our opinion, should be the topic of future research. Therefore a discussion of the models' respective advantages and disadvantages is in our opinion not within the scope of this paper.

Moreover, in this paper the model is just used to exemplify how the time and temperature dependence of the nucleated fraction depends on the standard deviation of the error function and the number of different surface sites on each particle. The discussion of the datasets by Shaw et al. (2005) and Niedermeier et al. (2010) is only qualitative. The authors did not attempt a quantitative fitting of the results because the

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system is under-determined. Nevertheless, a more rigorous discussion of literature data would add to the quality and value of the paper. Immersion freezing of ATD has been measured by several groups including Niedermeier et al. (2010), Marcolli et al. (2007) and Connolly et al. (2009). A thorough discussion of at least this IN should be attempted. In principle, all ATD immersion freezing data from different studies should be describable by the same contact angle distribution function. The authors should try to formulate such a function for their "soccer ball" model. It would also be interesting to see whether the contact angle distribution function of Marcolli et al. (2007) can be applied to the Niedermeier et al. (2010) data.

From the model results presented in the paper it is apparent that fitting the data from Niedermeier et al. (2010) as well as the data from Marcolli et al. (2007) and Connolly et al. (2009) (as the reviewer has suggested) is not enough to get valuable fit parameters since time dependent measurements are insufficient or not included in these studies. There is one recent study available dealing with both temperature and time depend measurements using relatively pure clay mineral particles. However, temperature and time dependent measurements used IN with different characteristics (e,g. size range) again making a meaningful fit difficult or impossible. In short, to our knowledge there currently seems to be no data set available sufficiently thorough as to distinguish between stochastic and singular aspects without making further model assumptions. This can therefore be taken as a suggestion for future work. And again, our main intention was to show conceptually the transition from stochastic to apparently singular behavior.

We added the following statement to the text: "Evaluation of the basic, fundamental features of the model (i.e., inherent stochastic nature of ice nucleation operating over a finite number of patches) challenges current experimental methods because it requires determining the freezing probability versus both time and temperature. For example, the frozen fraction vs. temperature curves for $\sigma_\theta = 0.001$ rad and 0.010 rad show a similar slope independent of n_{site} (see Fig. 5). But the $\ln \frac{N_u}{N_0}$ vs. time curves show different slopes depending on n_{site} (especially for $\sigma_\theta = 0.010$ rad, see Fig. 4). Furthermore fitting

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the frozen fractions of the ATD particles presented in Niedermeier et al. (2010) alone leads to an ambiguous result because in that case the system is under-determined, since the three parameters n_{site}, μ_θ and σ_θ can be combined differently to fit the frozen fraction. The different parameter choices, however, lead to very different time dependencies for the frozen fraction (see Fig. 7), which could be observed in an appropriately designed experiment. This implies that, in a hypothetical set of experiments aimed at fully characterizing the ice-nucleating properties of a population of particles, both temperature and nucleation time have to be varied, and particles with a size distribution as narrow and surface properties as uniform as possible need to be considered."

Specific comments

Page 3164, lines 16-18: Here the authors claim that the experiments are sufficiently controlled so as to allow interpretation with a simple model. However, I could not find an interpretation of the results of these experiments in the manuscript that makes real use of the model.

See above and the text has been changed to: "These are but two of a number of similar experiments carried out in various groups, but they are sufficiently controlled so as to allow clear interpretation in the context of the stochastic vs. singular controversy."

Page 3164, lines 24-25: Why can the modified singular hypothesis not explain these results? One active site on a particle that is described by Classical Nucleation Theory with a specific contact angle would lead to the observed fluctuations in temperature.

That sentence was wrong and has been deleted.

The nomenclature in equations (1) and (2) has to be improved: In equation (1), P is a function of T and the contact angle, in equation (2), however, only a function of T. Obviously, P is also a function of t. The frozen fraction should also be a function of T and t. The meaning of N0 is not explicitly stated.

We changed the nomenclature as suggested.

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Page 3170, lines 19 - 21: The authors assume that the curves become steeper with increasing number of sites because the stochastic behavior is recovered. However, the curves become also steeper because the contact angles of the best sites are becoming smaller and more similar with increasing number of sites. This explains also the shift of freezing temperature to higher values. It would be interesting to investigate how many of the best sites are responsible for freezing. This could be done by shutting off (1) all but the best site (2) all but the two best sites(3) all but the three best sites and so on, and then compare the frozen fraction for the different cases.

Concerning the first part of the question we added to the text: "The explanation for the curves becoming steeper is that the particles will exhibit sites with a similar range of contact angles as n_{site} increases. This behavior can also simply be interpreted as the 'recovery' of the stochastic behavior as discussed above."

As can be seen from figure 1 in the supplement, the smallest contact angle and therefore lowest energy barrier for ice embryo formation has the highest freezing probability.

This figure 1 will not be included in the text, but a corresponding paragraph was added to the text: "It is a fact that with increasing spread in the contact angle distribution function, and with increasing n_{site}, the probability that contact angles significantly smaller than the mean occur on various members of the particle population increases. With increasing σ_θ the smallest contact angle and therefore lowest energy barrier for ice embryo formation features the highest freezing probability, implying that more and more droplets will freeze at temperatures higher than that corresponding to the mean contact angle."

Page 3171, lines 14-15: where in Niedermeier et al. (2010) is the missing time dependence for freezing of ATD shown? This missing time dependence should be shown and discussed in this paper in more detail.

The original formulation was misleading. The text has been changed to: "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)."

Page 3171, lines 23-27: It would be interesting to see how different combinations of the fit parameters in the "soccer ball" model that are all able to describe the frozen fraction of the ATD particles in Niedermeier et al. (2010) influence the time dependencies of the frozen fraction. The authors should present such calculations in this manuscript.

We included such a figure (see figure 2 in the supplement which will be Fig. 7 in the paper) into the paper showing why "typical" data sets cannot be analyzed without further information. The text has been extended to: "Evaluation of the basic, fundamental features of the model (i.e., inherent stochastic nature of ice nucleation operating over a finite number of patches) challenges current experimental methods because it requires determining the freezing probability versus both time and temperature. For example, the frozen fraction vs. temperature curves for $\sigma_\theta =$0.001 rad and 0.010 rad show a similar slope independent of n_{site} (see Fig. 5). But the $\ln \frac{N_{\mathrm{u}}}{N_0}$ vs. time curves show different slopes depending on n_{site} (especially for $\sigma_\theta =$0.010 rad, see Fig. 4). Furthermore fitting the frozen fractions of the ATD particles presented in Niedermeier et al. (2010) alone leads to an ambiguous result because in that case the system is under-determined, since the three parameters n_{site}, μ_θ and σ_θ can be combined differently to fit the frozen fraction. The different parameter choices, however, lead to very different time dependencies for the frozen fraction (see Fig. 7), which could be observed in an appropriately designed experiment."

Figure 4: the y-axis in this Figure could be chosen better. Ln(Nu/N0) = -3 corresponds to an unfrozen fraction of 0.05. In the atmosphere and in the lab, such low unfrozen fractions are difficult to measure and are not very interesting. However, small frozen fractions are especially important for mixed phase clouds. This region of the Figure should be enlarged, especially in the panels (c) and (d).

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The region was enlarged as suggested but only for σ_θ =0.1 rad rad and 0.5 rad rad to preserve the straight lines for σ_θ =0.001 rad and 0.01 rad. (See new Fig. 4 in the supplement)

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