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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 1 for his comments. In the following the comments will be addressed and discussed.

Niedermeier et al. present a conceptual semi-quantitative model that attempts to explain observations of the ice nucleation ability of an aerosol made by two different techniques. This model works on the premise of dividing the surface into a number of equal-area sites; each being parameterized having a fixed and randomly chosen contact angle. Classical nucleation theory is used to compute the fraction of particles that is frozen as a function of the thermodynamic state and time.

The topic of the paper is appropriate for Atmospheric Chemistry and Physics and

of general interest to the Atmospheric Science community. However, I find that the manuscript is not sufficiently worked out to unequivocally endorse it for publication at this time. Specifically, I find that the authors have not taken the time and effort to really test their ideas but that they want to publish some untested ideas that will be elaborated upon in future papers. For example, the authors write "It is a separate question whether such an ensemble view reasonably captures the features of natural aerosol systems, and we leave detailed evaluation of that question for future work." As I argue below, I disagree that this is a separate question since the ideas inherent in the conceptual model are not really novel.

As succinctly outlined by the comments by Gabor Vali, the model presented here is not really new. The model is simply an implementation of ideas that pervaded the ice nucleation literature for the last six decades. Clearly heterogeneous ice nucleation cannot be completely stochastic since that would obviate the need of an ice nucleus. Equally clearly, ice nucleation is not completely deterministic as experiments of repeated drop freezing have demonstrated. The stochastic vs. singular debate is therefore more like the nature vs. nurture debate; both are important and their relative importance depends on the actual case considered. No convincing experiment or data is presented that sheds light on the actual mechanism of the nucleation process for ATD or aerosol samples in general. The manuscript simply posits a model and computes the implications without attempting to constrain the model with data. For this reason, the claim that this paper "bridges stochastic and singular behavior" is incorrect. The model simply highlights what behavior follows from what assumption.

With all due respect, but here we have to state that we don't agree with the reviewer. The main goal of the paper is to show that a purely stochastic model can produce singular behavior, and to illustrate, conceptually, the nature of the transition between the two limits. This, in our opinion, in itself is a new and original result worth publishing. The model is based on the well known fundamentals of classical nucleation theory, i.e. a theory widely used to explain both homogeneous and heterogeneous ice nucleation.

Furthermore, it represents an extension or modification of the well known and accepted models suggested by Marcolli et al. (2007) and Lüönd et al. (2010). We present the model as conceptual, and as stated in the paper we do not claim that it perfectly represents the behavior of realistic (complex) atmospheric ice nuclei. But we are confident that the model captures the basic behavior of the nucleation process. Doubting that, in our opinion, would imply doubting the applicability of CNT, a discussion we consider far beyond the scope of this paper. Finally, concerning the above criticism, we ourselves would like to quote Gabor Vali's comment stating: "This paper (N11) is a welcome contribution to the study of heterogeneous ice nucleation. The authors' endeavors to clarify the reasons for the dichotomy that prevails in the literature regarding the treatment of heterogeneous nucleation of ice, namely interpretations based either on stochasticity or on singularity." and at the end: "The above criticisms notwithstanding, this paper is a good step toward due recognition of the two inseparable aspects of ice nucleation."

This in itself does not merit rejection of the manuscript. It implies however, that the authors need to validate their model and present data and/or calculations that go beyond a mathematical implementation of a conceptual description of the ice nucleation process. For example, can the model be used to fit meaningful parameters to actual data? If this is done, is it consistent with all data collected to date? Do these parameters then make specific predictions that can be tested in further laboratory experiments or observational studies to verify or falsify the model? In my opinion the authors need to very explicitly point out how the model can be applied.

The model results presented in the paper demonstrate 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 suggested by e.g. reviewer 2) is not enough to get valuable fit parameters since time dependent measurements are insufficient or not included in these studies.

"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 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."

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. We have further illustrated this point in Fig. 1 in the supplement (this will be Fig. 7 in the manuscript) showing why "typical" data sets cannot be analyzed without further information. And again, our main intention was to explore the transition from stochastic to apparently singular behavior based on a set of relatively simple assumptions.

A second major criticism of the manuscript is the cherry picking of data. The authors qualitatively contrast studies by Niedermeier and Shaw (two of the authors), ignoring a vast body of ice nucleation literature on the same aerosol type. To have merit, a model/theory must be quantitatively consistent with all of the data, or it must be argued why some of the data are flawed or why it cannot be considered by the model.

Presumably there is enough diversity in the techniques to provide a span in nucleation time scales, specific aerosol surface area used and other important parameters to test if the model can be used to parameterize data and/or quantitatively explain the range of observations as the authors set out to do.

In this context it should be noted, that we by intention selected these two sets, one suggesting stochastic and the other singular behavior, and stated in the text that these are only examples. "The apparent conflict between these descriptions of nucleation is drawn into sharp focus by considering results from two ice nucleation experiments conducted by several of the authors. 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." We further cited other recent studies which show stochastic: (Seeley and Seidler, 2001a,b; Zobrist et al., 2007, e.g.,) and singular freezing behavior (Möhler et al., 2006; Connolly et al., 2009, e.g.,).

Concerning the model being "quantitatively consistent with all of the data", we would like to again state that according to our current knowledge, there is no consistent data set covering both temperature and time dependence of the heterogeneous nucleation process available (see also answers to the other reviewers).

To achieve such a description it is necessary to carefully evaluate the technique by which the ice nucleation activity was observed. There is significant uncertainty regarding the measured IN activity by different instruments and techniques; see special issue on the ice nucleation workshop in ACP ($http://www.atmos-chemphys.org/special_issue139.html$ *which also contains more ATD data for the authors to consider). Thus before the data presented here can be used to support theoretical claims, a self-consistent quality-controlled and validated dataset must be put together by the authors. Uncertainties must be included and potential biases must be discussed for all of the techniques.*

See above. It is our feeling that the suggested effort would take us very far from our intended objective of using a conceptual model to explore stochastic to singular behavior. It certainly should be a goal of future work, however, to produce data of sufficient quality and comprehensiveness to allow such a study to be undertaken.

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