Atmos. Chem. Phys. Discuss., 11, C1004–C1007, 2011
www.atmos-chem-phys-discuss.net/11/C1004/2011/

Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

Received and published: 21 March 2011

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) allow 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 as-

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sumes 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.

ACPD
11, C1004–C1007, 2011

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Finally, it is not clear to 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.

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 area. On each nucleus surface we assume a fixed number n_{site} 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. 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.

Case A: the population is completely uniform whenever $\sigma_\theta = 0$ independent of n_{site}.

Equation 1: P_{freeze} does not depend on the contact angle itself. It depends instead on the mean contact angle and the standard deviation.

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11, C1004–C1007, 2011

Interactive Comment

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-θ 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.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 3161, 2011.

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11, C1004–C1007, 2011

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