Atmos. Chem. Phys. Discuss., 11, C5397–C5402, 2011
www.atmos-chem-phys-discuss.net/11/C5397/2011/

Atmospheric Chemistry and Physics Discussions

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

D. Niedermeier et al.

niederm@tropos.de

Received and published: 24 June 2011

First of all we would like to thank Gabor Vali for his very interesting and valuable comments. We personally learned a lot about his insights into heterogeneous ice nucleation and hope the same holds for other members of the ice nucleation community. In the following his main comments will be addressed and discussed.

General Comments:

The magnitude of site-specific effects in N11 can be gauged from the differences induced by altering the width of the distribution of contact angles σ_θ. While not specifically stated in the paper, that spread can be deduced to be large for $\sigma_\theta > 0.1$ from the fact that in panels c and d of Fig. 4 of N11 temperatures many degrees higher

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

than the -21°C corresponding to $\sigma_\theta = 0$ are considered in order to see anything but instantaneous freezing.

This was already stated in the text, obviously not clearly enough. For clarification we included a figure (see Figure in the supplement, which will be Figure 6 in the manuscript) showing the mean freezing temperature, i.e., the temperature where 50% of the supercooled droplets are frozen, as function of σ_θ for $\mu_\theta = 1.0$ and nucleation time of one second.

So, it appears that there is no disagreement here between VS66 and N11.

According to our view, in an ideal model world the model suggested by Vali and Stansbury (1966) and the model introduced in this manuscript should lead to similar results although the models originate from different perspectives.

We added to or rewrote in the text:

"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"

"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."

The next point to examine is how different is the use of the contact angle to specify

ACPD

11, C5397–C5402, 2011

properties of a site from the characteristic temperature used in VS66. In my view, there is no fundamental difference since the contact angle serves in N11 to specify the properties of the sites by assigning a given $j_{\text{het}}(T, \theta_i)$ function to it. The characteristic temperature does the same by specifying a temperature at which $j_{\text{het}}(T, k, l, m)$ has a specific (threshold) value. The function is denoted here with k,l and m as unspecified factors meant to reflect the ice nucleation potential of the site. Those factors can be different for various types of sites (steps, dislocations, inclusions, inhomogeneities of any kind); usually these factors are not known. In practical terms, the characteristic temperature is close to the observable temperature of freezing on a site, independently of the assumed form of the $j_{\text{het}}(T, k, l, m)$ function, while $j_{\text{het}}(T, \theta_i)$ is a more abstract description. In all, whether the properties of a site are specified by the contact angle (N11) or by the characteristic temperature (VS66) there is a unique nucleation rate function attached to that site. This is also stated in point 3 of page 3166 of N11, using the word "characterize".

Qualitatively and maybe even quantitatively, both concepts should lead to similar results but in principle the models originate from different perspectives as mentioned above. However the question remains which parameter, contact angle θ or characteristic temperature T_c, is more useful for the description of het. ice nucleation. In general we developed the model based on CNT and in the context of CNT, contact angle is a well known and established parameter to describe ice nucleus surface properties and we therefore chose this parameter.

The foregoing two paragraphs demonstrate, I believe, that the N11 model is actually an implementation of the VS66 model.

See comments above

To underscore my main point, it may be useful to restate the results presented in N11 with the vocabulary of the VS66 model. The case of $\sigma_\theta = 0$ and $n_{\text{site}} = 1$ implies that all of the particles (one per drop) are identical, namely have the same characteristic

ACPD
11, C5397–C5402, 2011

Interactive Comment

temperature. If such a set of drops are held at a temperature where the rate of nucleation is relatively low (say, well below the characteristic temperature) there will be a decrease in the number of drops with time as shown in Fig. 3 of N11. The slopes of the lines in the graph will depend on the temperature difference between the temperature of observation and the characteristic temperature. No such experiment has in fact been carried out so far, because it is close to impossible to produce identical particles and place them one in each drop of water. The closest approach to this is to repeat many times the freezing of one sample, and those tests (e.g. Vonnegut and Baldwin 1984;Shaw, Durant and Mi 2005; Vali, 2008) indeed yield results reflecting the stochastic nature of nucleation on a site, though some alteration of the particle or of the site with time cannot be ruled out. If the number of sites is increased but are assumed to be identical ($\sigma_\theta = 0$ is maintained) a minor difference will develop depending on whether the site sizes decrease in inverse proportion to the number (fixed total area), as in the N11 model, or if the sites remain the same size, as could be the case with each site located on a different particle. In the former case, since the nucleation rate is expressed per unit area the increase in number is canceled by the decrease in size, leading to the same overall probability of freezing. In the latter case, the rate would increase in proportion to the number of sites and thus the slope of the line in Fig. 4a of N11 would increase. There would be no change from the stochastic pattern.

Concerning the last point we are in agreement. We modeled both situations, i.e., constant surface site size and decreasing site size with increasing site number per particle and gained the result suggested. However, as this was somewhat expected, we did not include this into the paper.

It follows from the aforesaid that the conclusion stated in the first three lines of Section 5 (page 3172) of N11 is incorrect. This also means that the descriptions 'transition' and 'bridging' are somewhat misleading. The two elements, site characteristics and nucleation rate, are always present and are always part and parcel of heterogeneous nucleation. One or other feature may become dominant depending on the sample be-

ACPD

11, C5397–C5402, 2011

ing examined and the experiment being performed. In other words, there are no two different types of heterogeneous ice nucleation, stochastic and singular, just a combination of the two. Experiments can reveal - or be designed to focus on - one or the other part of the picture but the two parts can never be separated. The results in N11 demonstrate this quite well by varying the magnitudes of the input parameters while leaving in place both of the processes involved. The above criticisms notwithstanding, this paper is a good step toward due recognition of the two inseparable aspects of ice nucleation. Hopefully the comments here presented will be helpful too. Yet, it should not be forgotten that, in spite of having clear concepts about the processes of heterogeneous ice nucleation, our understanding of the factors that control heterogeneous ice nucleation and our ability to predict nucleating potential as a function of substrate properties are very limited. Much remains to be discovered.

Here specific attention is drawn to the sentence, "The emergence of singular, or nearly singular behavior can be explained without appeal to active sites possessing characteristic (i.e., deterministic) freezing temperatures." We think most of the confusion appears to be a result of terminology: in the modified singular model "characteristic" denotes something like "threshold" temperature, whereas in our paper it is defined as deterministic — possessing no random feature. This is now stated in the text more clearly:

"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 be-

ACPD

11, C5397–C5402, 2011

Interactive Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

havior: 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."

Furthermore we changed the title of the paper to "Heterogeneous ice nucleation: Exploring the transition from stochastic to singular freezing behavior"

References

Vali, G. and Stansbury, E.: Time-dependent characteristics of the heterogeneous nucleation of ice. Can. J. Phys., 44(3), 477–502, 1966.

Vali, G.: Freezing rate due to heterogneous nucleation, J. Atmos. Sci., 51(13), 1843–1856, 1994.

Vali, G.: Repeatability and randomness in heterogeneous freezing nucleation, Atmos. Chem. Phys., 8, 5017–5031, 2008.

ACPD

11, C5397–C5402, 2011

Interactive Comment