Atmos. Chem. Phys. Discuss., 15, C3612–C3617, 2015
www.atmos-chem-phys-discuss.net/15/C3612/2015/


Atmospheric Chemistry and Physics Discussions

# *Interactive comment on* "Analysis of isothermal and cooling rate dependent immersion freezing by a unifying stochastic ice nucleation model" *by* P. A. Alpert and D. A. Knopf

**G. Vali**

vali@uwyo.edu

Received and published: 15 June 2015

[acp, ms]copernicus



## Stochastic versus site-specific interpretations

G. Vali

15 June 2015

This paper by Alpert and Knopf (2015; AK15) shows how experimental results involving different substances and different measurement techniques, can be reproduced by Monte Carlo simulations that use $J_{\text{het}}$ (cm$^{-2}$s$^{-1}$) as a function of temperature only (for given materials) and the surface areas of the INPs in individual drops are assumed to follow lognormal distributions. Underlying the AK15 model is the assumption that $J_{\text{het}}$ fully specifies the nucleating ability of a material, i.e. surfaces are uniform with respect to their potential to promote ice nucleation, and no sites with special properties need to be considered. Hence, the model employs the stochastic description of ice nucleation. That assumption is compared in what follows here with the site-specific interpretation[1] to show that both descriptions offer plausible explanations for key experimental results and that more complex data sets and more comprehensive analyses are needed in order to effectively distinguish between alternative explanations.

The results shown in Fig. 1(A) of AK15 provide a good example for considering the two

[1]The terminology and the abbreviations used in this note follow that given in http://www.atmos-chem-phys-discuss.net/14/C13082/2015/acpd-14-C13082-2015.pdf. Where appropriate, the notation of AK15 is used.

alternative views. This graph shows the fraction of drops remaining unfrozen after time $t$ in an isothermal experiment[2]. As seen in the graph, the fraction of drops remaining unfrozen, $f_{\text{ufz}}$, follows an exponential decay if all drops are assumed to contain the same amount of INP surface area. In contrast, the magnitude of the slope of the curve diminishes with time if the surface area distribution is non-uniform. This same difference between constant decay rate versus decreasing decay rate was argued in Vali (2014; V14) to indicate agreement with a stochastic description versus the site-specific description of Vali and Stansbury (1966, VS66). Herbert et al. (2014; H14) showed that the decreasing pattern can also be reproduced by the multi-component model that assumes a range of values for the nucleation rate coefficient for the same material. For this discussion, the VS66 and the H14 descriptions can be viewed as expressing the same concept, i.e. that sites of different effectiveness exist for given samples. Thus, we have two alternative explanations for the same pattern: site variations and size variations, that is qualitative or quantitative reasons for differences in nucleation probability. In essence, both descriptions see the slowing rate of freezing as a result of a rapid exhaustion of drops with greater chance of freezing. Both descriptions rely on adjustable parameters to fit the data.

AK15 ascribes the decreased probability to the fact that some drops have INPs with smaller surface areas $A_j$ in them so that $J_{\text{het}} \cdot A_j$ is lower and a longer time is required for an event to occur. The exact manner of decrease of $f_{\text{unf}}$ depends on the shape of the particle size distribution. Given sufficiently long time, $f_{\text{unf}}$ will tend to zero for any realistic size distribution of INPs if all drops contain at least one INP.

In the VS66 description, each site is seen as having a different site nucleation rate $J_{\text{het},T^c}(T)$ attached to it with all relevant values of the function falling within a narrow range of temperatures. The abundance of sites is given by number density functions

[2]In fact, analysis of such an experiment would have to account for drops frozen during cooling to the selected test temperature. This is ignored in AK15.



$n_s(T^c)$ or $K(T^c)$ where $T^c$ are the characteristic temperatures of the sites[3]; these quantities scale with INP content. The vary rapid variation of $J_{\text{het},T^c}(T)$ means that at any given temperature only a limited number of contributions are expected to the number events observed from drops containing randomly distributed sites. Thus, the $f_{\text{unf}}$ curve levels off after some time at a value other than zero. The exact form of the decrease in $f_{\text{unf}}$ depends both on $J_{\text{het},T^c}(T)$ and on $n_s(T_c)$.

It seems clear that both the AK15 and VS66 models are capable of providing a rationale for the shape of the $f_{\text{unf}}$ curve in Fig. 1 for $\sigma_g = 10$ in AK15. This is so because the decay rate in both models is governed by the time rate of decreases of the product of nucleation rate times surface area within the unfrozen population of drops. In AK15 the decrease is due entirely to the falloff of particle surface area in the unfrozen drops, i.e. the tail of the log-normal distribution assumed in AK15. In VS66 the main effect is the decrease in the number of unfrozen drops that contain INPs with sites that have appreciable values of $J_{\text{het},T^c}(T)$ at the test temperature. This function is not known with precision at this time; evidence points to rapidly decreasing values for $T > T^c$, perhaps by factors of about $10^2$ for each degree difference in ($T - T^c$).

A common factor in all models is the number distribution of INPs expressed by $n_s(T)$, $n_s(T^c)$ or $K(T^c)$. These quantities are dependent on the composition and size distribution of particles and on other possible factors that influence their surface properties. Since this number distribution can only be determined empirically, critical tests have to focus on the determination of the nucleation rate coefficient or site nucleation rate, more specifically, on the rate of change of these quantities with temperature. With the stochastic model (no size dispersion, single component) the freezing rate observed as a function of temperature, $R(T)$, is interpreted as the nucleation rate coefficient times the surface area of INP per drop, $J_{\text{het}}^{\text{apparent}}(T) \cdot A$. As shown in V14, the temperature-dependence of this quantity can be approximated by exponential

[3]Assuming the form of the function to be the same for all sites, each site can be defined by the characteristic temperature at which $J_{\text{het},T^c}(T)$ has a given value. (cf. V14). Definitions of the symbols are those used in V14.

functions with $\omega_{\text{stoch}} = -\frac{\mathrm{d}(\ln J_{\text{het}})}{\mathrm{d}T}$ in the range 0.5 to 1. For homogeneous nucleation $\omega_{\text{hom}} = -\frac{\mathrm{d}(\ln J_{\text{hom}})}{\mathrm{d}T}$, and for the site-specific description $\omega_{\text{site}} = -\frac{\mathrm{d}(\ln J_{\text{het},T_c})}{\mathrm{d}T}$ values are in the range 3 to 5. Data for $\omega_{\text{stoch}}$ and $\omega_{\text{hom}}$ are given in Table 1 of V14; the value for $\omega_{\text{site}}$ is a rough estimate discussed in Section 5.1 of V14.

The results in AK15 for experiments with cooling at constant rates show that the assumption of non-uniform INP sizes leads to nucleation rate coefficients (called "actual rates" in AK15) whose temperature variation is greater than for uniform sizes ("apparent rates" in AK15) by about factors of two: $\frac{\omega^{\text{actual}}}{\omega^{\text{apparent}}} \approx 2$ in Figs. 5 and 6, with $\omega^{\text{actual}} \approx 2$ and $\approx 1$ respectively. Specially the first of these values is closer to, but still considerably lower, than the values quoted in the preceding paragraph.

As the foregoing shows, comparisons of $\omega$-values indicated by different assumptions can provide a basis for evaluating models. A weakness of this approach, at the moment, is the paucity of data for $\omega_{\text{site}}$.

Other possible avenues for the evaluation of models is to use, as can be seen in the examples given by Herbert et al. (2014), different types of experiments with the same sample. Comparisons of the results of tests at constant temperatures, time to freeze for individual drops, the scatter in freezing temperatures on repeated trials, experiments with steady cooling and with small intervals of warming interspersed, all with different materials, have the potential to provide improved understanding of heterogeneous ice nucleation.

The valuable contribution of AK15 is to demonstrate the importance of basing all model calculations on realistic particle size distributions. It may be added that, rather than assuming that all surfaces of a given substance have equal potential to promote ice nucleation, the proportionality of site frequencies to particle surface area should be be tested explicitly for the whole range of particle sizes present in experiments. There are reasons to question whether particles of different sizes have nucleating potentials in proportions to their surface areas and over what range of sizes that assumption may



hold up. Also, the temperatures for which the proportionality assumption holds can be expected to be critical. In all, it is clear that the AK15 model points to a factor not to be ignored in future analyses of data, but it leaves open the question of validity of the stochastic interpretation versus a site-specific one.

## References

Alpert, P. A., and Knopf, D. A.: Analysis of isothermal and cooling rate dependent immersion freezing by a unifying stochastic ice nucleation model, Atmos. Chem. Phys. Discuss., 15, 13109-13166, 10.5194/acpd-15-13109-2015, 2015.

Herbert, R. J., Murray, B. J., Whale, T. F., Dobbie, S. J., and Atkinson, J. D.: Representing time-dependent freezing behaviour in immersion mode ice nucleation, Atmos. Chem. Phys., 14, 8501–8520, 2014, doi:10.5194/acp-14-8501-2014.

Vali, G.: Interpretation of freezing nucleation experiments: singular and stochastic; sites and surfaces. Atmos. Chem. Phys., 14, 5271–5294, doi:10.5194/acp-14-5271-2014, 2014

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