Response to Gabor Vali:

We thank Gabor Vali for this synopsis. The comments are copied below followed by our responses in bold.

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 Jhet (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 Jhet 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.

[1]The terminology and the abbreviations used in this note follow that given in http://www.atmos-chem-physdiscuss.net/14/C13082/2015/acpd-14-C13082-2015.pdf.

The points raised by Vali are summarized concisely; however, there are two that need minor clarification. First is that we do not assume INP surfaces are uniform. Our results are in accord with the notion that many active sites with different ice nucleating abilities may be present on the surface (e.g. Broadley et al., 2012, Vali, 2008). We assume a particle-type specific J_{het}. We clarify this in our general response and our response to reviewer #1. However, we hypothesize that the variability in ISA per droplet, which is clearly detailed in some immersion freezing studies (e.g. Broadley et al., 2012; Wright and Petters, 2013), may be sufficient to explain the non-exponential frozen fraction with time in isothermal nucleation experiments, and the apparent cooling rate and surface area dependence on J_{het}.

Second, we agree with Vali that more comprehensive analyses are needed in future immersion freezing studies. Clearly, our model results suggest how to improve future ice nucleation experiments and analyses. Specifically, there is the need to increase droplet numbers and number of experimental trials, and make accurate ISA measurements and measurement of ISA variability per droplet for a better understanding of the immersion freezing data.

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

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.

[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.

We appreciate the comment and agree in general with this assessment. However, strictly speaking our model does not represent an alternative to these descriptions. Rather, our model suggests the possibility that experimental droplet to droplet variability in ISA and ice active sites may act together where the latter is assumed to result in internally mixed INPs (Broadley et al., 2012). We find that quoted ISA variability in Wright and Petters (2013) and Broadley et al. (2012) is sufficient to represent the experimental immersion freezing data. This implies that the effect of droplet to droplet active sites variability should be small by comparison.

It is important to note that no fitting parameters are required in our model. The individual ISA per droplet, the number of droplets used in an experiment, N_{tot}, and the heterogeneous ice nucleation rate coefficient, J_{het}, are all measureable parameters and all that are required for the model. Temperature, T, and time, t, are the only independent variables considered in the model. If the ISA per each droplet is not known, then a median (or average) ISA per droplet, A_g, and standard deviation of the ISA per droplet, σ_g, can be measured and used. These physical parameters are only required to be fitted when this information is not given by an experimental study.

AK15 ascribes the decreased probability to the fact that some drops have INPs with smaller surface areas Aj in them so that Jhet · Aj is lower and a longer time is required for an event to occur. The exact manner of decrease of funf depends on the shape of the particle size distribution. Given sufficiently long time, funf 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 $J_{het,Tc}$ (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 $n_s(T_c)$ 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 $J_{het,Tc}$ (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 funf curve levels off after some time at a value other than zero. The exact form of the decrease in funf depends both on $J_{het,Tc}$ (T) and on $n_s(T_c)$.

[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 $J_{het,Tc}$ (T) has a given value. (cf. V14). Definitions of the symbols are those used in V14.

It seems clear that both the AK15 and VS66 models are capable of providing a rationale for the shape of the funf curve in Fig. 1 for σg = 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 $J_{het,Tc}$ (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 102 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, $J^{apparent}_{het}$ (T) · A. As shown in V14, the temperature-dependence of this quantity can be approximated by exponential functions with $\omega_{stoch} = -d(\ln J_{het}) dT$ in the range 0.5 to 1. For homogeneous nucleation $\omega_{hom} = -d(\ln J_{hom}) dT$, and for the site-specific description $\omega_{site} = -d(\ln J_{het,Tc}) dT$ values are in the range 3 to 5. Data for ω_{stoch} and ω_{hom} are given in Table 1 of V14; the value for ω_{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: ω actual ωapparent ≈ 2 in Figs. 5 and 6, with ω actual ≈ 2 and ≈ 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 ω-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 ωsite.

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.

We greatly appreciate the comments by Gabor Vali and recognize the discussion points raised as very important to consider for future studies. Vali states that surface area variability or site variability should be tested in immersion freezing experiments, and we agree. A much better understanding of the physicochemical properties of active sites is necessary to prove or falsify the concept of single active sites initiating ice nucleation. Our goal in this study was to represent immersion freezing data using only physical observables and classical nucleation theory. The successful representation of the experimental data by our model challenges how we think about active sites on particles and, hopefully in line with Vali's comment, motivates novel experimental investigation which will resolve the role of active sites in heterogeneous ice nucleation.

References:

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