Referee comment on revised manuscript by Hassan Beydoun, Michael Polen and Ryan C. Sullivan

Gabor Vali

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The wording and use of symbols here follow Vali et al. (2015).

1 The problem of INP apportioning in drops (as I see it).

Freezing nucleation experiments with drops of uniform sizes and with equally distributed, known quantities of suspended material are evaluated in terms of some variants of Eq. (12) in Vali (2014) in many publications, including the one under discussion. The resulting $n_s(T)$ functions, or nucleus spectra, are considered good representations of the ice nucleating potential of the material examined. However, two additional factors have to be taken into account when the spectra are used in a predictive mode, i.e. applied to estimate freezing of drops of different sizes and with different concentrations of the material. These additional factors are, first, that the suspended material consists of particles of determinate sizes, and, second, that nucleating sites have finite dimensions and may require even larger areas around them to perform. Particle sizes can, in principle, be determined. Site areas are not well known.

One issue arising from the factors just described is how nucleating sites are apportioned among drops when the average number of sites per drop is low and an unequal distribution of the number of sites can be expected. Such low numbers are bound to be the reality for sites active at higher temperatures, the scarcity gradually increasing with increasing temperatures. This is a fairly straightforward problem to address via the Poisson distribution, either in terms of total surface area expected per drop, or in terms of the number of INPs (Vali, 1971). Particle sizes and the average number of particles per drop need to be known if surface rather than number of INPs is used. It is prudent that the $n_s(T)$ or K(T) spectra be applied only over the range for which it has been derived from experiment, i. e. not to extrapolate algebraic representations of the spectrum.

The possibility that particle sizes become too small to contain nucleating sites is more difficult problem. It can probably be addressed with experiments using particles of different sizes, but, as far as I know, such experiments have not been possible so far with particles small enough for the limit to be reached. Theoretical estimates of the dimensions required for nucleating sites of different degrees of activity are not reliable, though models of molecular clustering are beginning to provide some indications.

2 The approach of Beydoun et al. and its critique

The paper develops a scheme for dealing with the issue of small average particle surface area per drop. Another problem, a saturation effect, is also considered but that is not a real issue, in my opinion.

Whether the approach of this paper is better – more practical, more intuitive etc. – than the one sketched in the first part of this comment can be judged by examining the details of the method proposed in this paper. This view already incorporates the judgement that the proposed theory does not present new insights but is a procedure to improve data interpretation. Thus, the origin of the assessment of ice nucleating ability comes from experiment, not theory.

It may be useful to restate what I understand to be the tenets of this paper. The paper states that it is based on classical nucleation theory (CNT). As an aside, I note that this is a somewhat hollow claim, since the thermodynamic or kinetic aspects of that theory are not tested, nor do they impact the analyses done. A rate equation analogous to Eq. 13 in Vali (2014) is used with contact angle as the measure of effectiveness. A normal distribution of contact angles, $g(\theta)$, is assumed, similarly to other publications. As a next step, in section 3.2 the distribution is limited by upper and lower limits θ_{c1} and θ_{c2} . The details of this process are, for me, the most obscure part of the paper. In principle, the resulting P_f probability function defines a spectrum of activity and serves the same purpose as the K(T) or $n_s(T)$ spectra.

To describe the diminishing probability of finding nucleating sites in a drop, this paper introduces the concepts of external versus internal variability and the notion of a critical area. External variation arises when the particle surface area is reduced so that the full range of internal variation of INP effectiveness is not realized. The assumption of a normal distribution, which by definition is continuous to infinity at both ends, leads to the need for the critical area and critical contact angle range concepts. Below the critical area threshold, randomly sampled different g-distributions account for different experimental sets.

The fit shown in Fig. 1 by applying a distribution of contact angles (activity values), as opposed to using a single value of the contact angle, is the first support given for the proposed scheme. Again, this has been shown already in other papers. Also, the fit isn't really significant unless it is tested against empirical data for a number of different cooling rates. The emphasis of Section 3.1 of the paper is that a single particle is used for repeated tests, thus excluding external variability among drops. A number of other experiments of this kind have been described in Vali (2014, Section 3.1.2) and also discussed in Vali (2008) and Wright and Petters (2013). Reasons for the spread of observed freezing temperatures are interpreted there, and supported by other publications, as a

combination of time-dependence (stochasticity) and possible alterations of the particle surface. The prediction in Fig. 1 for a 1-h holding time is not supported by evidence, in fact it is contrary to data reviewed in Vali (2014, Section 3.2.2) and Vali and Snider (2015, Section 2.3).

The main support for the critical area concept is seen in improved fits to fraction frozen curves for samples at low particle concentrations. When viewed in terms of $n_s(T)$ spectra, in Fig. 11, it is seen that gradually higher concentration values are derived as the particle loading is reduced. The upward shift for the Broadley et al. (2012) data set is almost inversely proportional to the increase in indicated surface area over a factor 30 change. For the CMU data set it is much less, about a factor 30 for a 500-fold decrease in loading. Each of these differences is smaller than the range of concentrations covered by data from any one of the samples, and the two data sets form a roughly consistent band covering eight orders of magnitude, also overlapping the data from Hiranuma et al. (2015). This broad consistency makes it seem somewhat secondary that within each set of experiments there is a trend toward higher n_s values with lower particle loading. Yet those trends are clear. While I find many faults with the critical area explanation of this paper, it does achieve a degree of success in rationalizing the effect. Looking at Fig. 11, it is less clear to me how the authors see a change only past a certain critical value. It should be noted that the scatter of data for any single experiment introduces considerable subjectivity in judging the quality of fitted functions and in the comparisons of different runs. Consequently, conclusions need to be read with caution.

The critical area notion introduced in this paper is similar to the idea expressed in Bradley et al. (2012) saying that "It appears that NX illite contains a rare particle/nucleation site type which dominates the freezing process when the overall surface area is greater than $\sim 2 \cdot 10^{-6} \text{cm}^2$ per droplet." Interestingly this quote leaves it open that a different particle type is involved, as if the powder used in the tests contained a low proportion of some other material or other form of illite. In either case, it isn't easy to see a plausible reason for such critical value threshold phenomena in connection with ice nucleation. So, the arguments given in the paper (page 22, lines 10-20) about settling and coagulation of particles reducing the area effectively available for presenting nucleation sites do make some sense, though water would be still in contact with the particle surfaces even if aggregated into clumps and nucleation is not certain to be inhibited.

Regarding the claimed saturation effect, I find the data less then convincing (considering potential errors) and the notion is counterintuitive, as I argued in the second comment I made on the first version of the paper (http://www.atmos-chem-phys-discuss.net/acp-2015-1013/acp-2015-1013-RC2-supplement.pdf). Can the critical area values derived in the paper be given any meaning in terms of interpretation, significance, comparison to other characteristics of the materials tested? If the activity of the INPs is a continuous function - with decreasing frequency toward higher temperatures - how can saturation (page 12 bottom) be achieved? A truncation of potential activity (at some θ value for this model) would be required for saturation to be realized. Do the authors have evidence to support that assumption? The data shown in Fig. 8 are not convincing for a

saturation effect since the lower portions of the fraction frozen curves move to higher temperatures as the particle loading is increased.

3 Specific points.

Empirical data are used without any consideration of error ranges from limited sample sizes. This is specially serious at the upper end of the temperature range for each experimental run. It is conceivable that many of the discrepancies whose root cause is being examined in the paper arise from statistical uncertainties in the reported data. Having no objective measures of goodness of fit and weighting factors for data points from single runs leave most comparisons subjective. Multiple repetitions of the experiments would have been needed to increase the reliability of the data.

Other procedural errors – solute effects, coagulation rates, settling, aging, background, etc. – also enter as samples of different particle loading are prepared. The authors themselves cite such processes as possible explanations for the high versus low particle loading observations.

The solution of Eq. (9) to yield a fit for $g(\theta)$ needed some assumptions about $J(T, \theta)$ and that is not described in the paper. The exercise presented in Section 3.1 for a 1-h holding time is confusing, since it is unclear what the authors mean by "running Eq. (7) for the entire temperature range ..." (page 9, line 14).

Reference for each item in the following list is by (page number)/(line numbers).

- 3/18 More likely 2014 instead of 2008.
- 3/20-27: There is a lot of vacillation in these sentences regarding the importance of time-dependence. More specific results are available in the literature. In line 21, "temperature fluctuations" is a poor choice of words for what the authors wish to say.
- 3/... Alpert and Knopf (2016) should be referenced and their approach contrasted with the one in this paper.
- 4/16 What insights have been derived?
- 6/5: It is incorrect to reference Vali (2008) as a source for Eq. (3) using J(T) in the exponent. The similar equation in Vali (2008) is in terms of n(T) which is time-independent. Eq. (3) implies that A and t have equivalent impacts, i.e. that a doubling of the surface area would produce the same result as a doubling of the time spent at some temperature T. This is not supported by evidence as the authors summarize on page 3. Anyway, the assumption of constant cooling rate eliminates the time variable going from Eq. (8) to (9).
- 7/5-6 Seems to contradict what is said later on (23/24-28).
- 8/8 ... There are several data sets presented in the referenced paper for volcanic ash. Which one was used here and why?

- 7/15-17: Is the meaning of "nucleating species" and "type" the same?
- 11/22 What is meant by capturing "99.9% of the complete freezing probability"?
- 13/6 What is meant by "surface area density"?
- 15/20-23 The brevity of this description of the origins of new data that were added in this version of the paper is welcome, but sample sizes (drop numbers), the origin of the illite sample and other essential details should have been given.
- 20/15-19 How is it possible that the same trend in the right hand plots of Figs. 6 and 7 (shift to left for decreasing concentrations) leads to an downward order in Fig. 6b and the opposite in Fig 7b? Both samples are seen in the left hand plots to have decreasing activity with decreasing concentration, not just Snowmax, as claimed in the sentence later on this paragraph (20/26-27). Is there a data processing problem here?
- 23/10-11 Perhaps you meant "... not to have a single ..."
- 25/25-28 The argument here seems backwards, as more active (low-contact angle) sites are less frequent and they can be assumed to be larger than less active ones.
- 26/13-15 How exactly does a "narrow range" explain the reverse trend in n_m for Snowmax?

4 Summary.

Changes made since the first version of the paper improved the readability of the paper but it still contains many parts that are difficult to follow and are overly speculative. Only a selection of these hazy passages are listed in the foregoing sections.

The paper focuses on the problem of apportioning of INP particles or sites among drops in freezing experiments. The problem has come to attention because of some apparent irregularities the results derived from series of experiments with varying particle concentrations. Examination of these irregularities leaves some questions not addressed in the paper and are taken too readily as starting points for the development of the new critical area parameter. Conceptually, the problem makes sense but with all factors (nucleating site dimension, particle size distribution, possible mixtures of components of different properties) being continuous variables it is difficult to justify threshold values. It is counterintuitive that "high" and "low" surface area values would exhibit different characteristics such as slope changes, cooling-rate dependence (in Broadley et al. 2012) and critical area thresholds.

In all, the paper starts with the realistic idea of a spectrum of activity for nucleating sites for every particle, but presents an overly complex numerical procedure for fitting empirical data and introduces concepts that seem forced in comparison to other published approaches. In the hands of the authors the procedure yielded some agreements with selected data sets, but many details of the procedure are obscure. It is unlikely that the procedures reported in the paper could be independently reproduced by others, as the usual criterion for scientific works demands. That the paper could perhaps be the basis for other, more readily acceptable treatments is a possibility. More robust data would also be desirable before formulation of explanations for minor aspects of the data.

5 References

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