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Interactive comment on "Generalisation of Levine's prediction for the distribution of freezing temperatures of droplets: a general singular model for ice nucleation" *by* R. P. Sear

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The author of this paper has gone back over half a century and extends ideas put forth then in a short and difficult-to-find paper. There is special merit in this look back to history because it breaks the myopia of following only the latest works in a field. The re-cast results have added usefulness.

Levine's 1950 paper provided a concise and plausible theory for ice nucleation in small volumes of water drawn from the same source. The original motivation for the work was to interpret the laboratory experiments of his colleagues Dorsch and Hacker (1950), all aimed at understanding aircraft icing. Curiously, Levin's analysis didn't really apply to

the experiments it intended to explain, since droplets in those experiments were produced by condensation from the vapor, not drawn from a larger (bulk) volume. However, the droplets rested on a platinum surface and that makes the theory relevant if that surface provided the nucleating sites. In any case, Levin's ideas were consistent not only with the experiments it addressed directly, but also with a larger body of observations by Dorsey (1938) and many others. Subsequently, Levin's theory formed the basis for the work of Langham and Mason (1958), and yet later for that of Vali and Stansbury (1966) who named the theory the "singular hypothesis".

Sear's re-examination of the Levin theory - the singular model - comes at a time when there is considerable debate about the relative merits of that model versus the stochastic model (Bigg, 1953). As argued by Vali (1994, 2008, 2010, 2011, 2012) the singular model is a good first approximation, useful for the analysis of data derived from experiments in which cooling is steady.

In addition to the above remarks amplifying the historical perspective not well covered in Sear's paper, two specific issues are raised in the following.

1. As done by Langham and Mason (1958), Vali (1971; V71) and others, the chance allocation of each type of nucleating site among many droplets can be described by a Poisson distribution, so that the probability, p, of finding at least one site of type n(T) in a droplet of volume V is given by p = 1- exp(-Vn) where n(T) is the number of sites of that type per unit volume in the bulk liquid. The value of n(T) is only a function of temperature in terms of the singular model. The important assumption here is that all of the sites are rare occurrences residing on separate particles so that they can end up in different drops. The other well-accepted assumption is that only one site is needed to produce nucleation.

If the singular model is to be applied to experimental results, information about n(T) can be obtained based on the above. This information is the nucleus spectrum as described in V71. The spectrum, in other words the distribution n(T), is found to be exponential only in some cases. For those samples, a logarithmic dependence of median freezing temperature on droplet volume can be derived. This appears to be in agreement with Sear's findings for the Gumbel distribution (eq. 7 and Fig. 2). However, samples of atmospheric precipitation and those with introduced impurities often show strong deviations from the exponential.

The treatment based on the Poisson distribution does not require n(T) to have any specific form. The three models presented by Sear each imply some prescribed form, or at least general trend of n(T) toward high values of T.

In essence, the goal of all these analyses (models) is to quantify and characterize the ice nucleating sites. One could say that these are backward models of the process, in contrast to what a forward model would be if the model could build on descriptions of molecular configurations on the surfaces of particles and of ice embryos. The so-called classical nucleation theory, with its use of thermodynamic parameters, is somewhere between these limits. How much does one actually learn from these backward models? Sear sees utility in assessing the form of n(T) when dealing with samples containing a known type of impurity. Indeed, some authors tie n(T) to measures such as contact angle or size using the spherical cap thermodynamic theory. In reality this just shifts the measure of activity to another parameter of dubious relevance. The results of the unconstrained derivation of n(T) - the nucleus spectra -are purely empirical; these spectra can be tied to the chemical or physical state of the impurities carrying the nucleating sites by comparisons with prepared samples and with additional tests. All of these are difficult and uncertain prospects.

Sear suggests that data should be tested against the GEV distributions and that the assumptions of the singular model can be decoupled from the assumptions of an exponential n(T). I agree with the general thought behind this suggestion, but want to emphasize that there are many other tests possible, and have been already done, to accomplish that goal. Deviations from the singular model due to time-dependence (stochastic effects) have been shown to be real but of relatively small magnitude. For

example, VS66 reports a change of about half a degree in mean freezing temperature for an order of magnitude change in the rate of cooling. More significant time dependent effects can be observed with the temperature held constant. A practical implication of the aforesaid is that, for example, in comparing experimental results for different materials, or testing against the GEV predictions, a uniform and constant rate of cooling must be assured. Variations and non-linearity of the temperature-time function will distort the resulting frequency distributions of freezing temperatures.

2. Levine's assumptions are re-stated by Sear. It is unclear to me whether they are really the same. Since the words used to talk about these matters have changed over time, special care is needed.

In Levine's own words: "An assumptions is made that a large number of motes are present in liquid water. Also, each mote is assumed to be associated with a definite spontaneous freezing temperature. The freezing temperature of a water sample is governed by the mote in the sample that is associated with the highest freezing temperature." To implement these assumptions, Levin goes on to calculate the probability distribution of how motes of a given kind may be distributed by chance into small volumes drawn from the original sample, combined with the probability that there are no motes associated with even higher freezing temperatures.

Sear's description of these assumptions (page 10503, line 2) starts with considering " a set of nominally identical liquid water droplets" and continues with (same page, line 16): "Each droplet contains impurities that have a total of N nucleation sites."

Levine does not constrain the total number of sites (motes) in each droplet (small volume) but allows the number available in the original (bulk) sample to be divided by chance into each droplet. The consequences of this difference in the mathematical formulation are subtle and beyond my expertise. Perhaps the actual formulation of Sear's model makes the two assumptions equivalent, but if so, the author should clarify that.

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