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Interactive Comment

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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I am grateful to both Prof Vali and the anonymous referee 2 for their reports. In response to their helpful comments and suggestions, I have made changes which I believe have improved the paper. Below, I outline these changes and reply to their comments. I will start with Prof Vali's comments.

I would like to thank Prof Vali for his helpful comments. His comments on the history of what he christened the "singular hypothesis" are particularly useful. I have amended the second paragraph of the Introduction, to note that the name "singular"is due to Vali and Stansbury. I also absolutely agree with Vali's description of the singular model as "good first approximation". I think that is exactly what it is. In addition to these historical notes, two specific issues were raised. I will address these in turn.

1. I agree with the Poisson functional form discussed here, it is the same as my Eq. (11). As he states, this Poisson form is very general. Also, as he states this distribution does not specify the form of the function he denotes by $n(T)$. An advantage of extreme-value statistics is that it makes testable predictions for the temperature dependence of the fraction of droplets frozen. Finally, I thank the referee for his useful comments on experimental work on testing the assumptions in singular models.

2. Levine's and my assumptions lead to (almost) the same mathematical expression, as I explain in Appendix A. So when experimental data is fit the results will be very similar, although my formula is a little cleaner and so simpler. This is so when we assume that the number of sites is assumed proportional to volume, $N \propto V$. If this is not assumed the formulae are mathematically almost the same but use different variables (N and ΔV). However, we are both assuming that the number of nucleation sites is the same in the droplets.

   So, it is correct to say that I assume N is fixed. There can be a difference between assuming N is fixed, and assuming V plus the average number density of sites are fixed. If each nucleation site is on a different *independent* impurity particle, and these impurity particles are present at a concentration c then the average number of impurities is $\langle N \rangle = c\Delta V$, and the size of the fluctuations around this mean is $\sigma = (\langle N \rangle)^{1/2}$, where I have used the central limit theorem of statistics. For large $\langle N \rangle$ these fluctuations are then negligible.

   In all but extremely small droplets, the total number of nucleation sites $\langle N \rangle$ is likely to be very large. However, if great efforts have been made to purify the water this may not be so. A more common problem with assuming N is the same

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for all droplets is probably that the impurities are mostly on some small number of particles, $n \ll N$. Then the fractional size of the fluctuations in N about its mean value is of order $n^{-1/2}$. So, if in droplets n is small, then this could potentially cause deviations from the generalised extreme-value (GEV) distribution, due to some droplets having more nucleation sites than others.

I would like to thank the referee for this stimulating comment. For the paper, I have added a new subsection 4.4, that discusses possible variations in N from droplet to droplet. This is referred to at the start (second paragraph) of section 4, and as an additional reason (number 4) for deviations from the GEV in paragraph 4 of the conclusion (section 5).

Now I would like to turn to the report of anonymous referee 2. I would like to thank the anonymous referee 2 for their helpful comments. I am happy to elaborate on the two points the referee mentions:

1. The Weibull model does indeed imply a hard upper limit to the temperature (my T_U) at which there is nucleation. The prediction is that above this temperature, even for an infinite number of nucleation sites, there is no nucleation.

   In reality there cannot be an absolutely sharp upper cuttoff. However in practice, the Weibull model should be a good model for experimental data when the inevitable uncertainty in T_U, call it δT_U, is much smaller than the range of temperatures over which nucleation occurs. This range of temperatures could be measured by the standard deviation of the observed nucleation temperatures, σ_F. So when $\delta T_U \ll \sigma_F$, and the Weibull model fits the data well, the Weibull model should be useful.

   I have added a new short paragraph to the manuscript, to discuss this point. The paragraph is between Eqs. (14) and (15). I have also added two sentences to the

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end of the paragraph containing Eq. (17), to discuss how this affects the Weibull prediction for the scaling of the median freezing temperature with size.

As the referee comments, classical nucleation theory predicts that the nucleation rate is only zero at 0 C. Below that it is non-zero. However, it can be extremely small. As 0 C is approached from below classical nucleation theory predicts that the free energy barrier to nucleation diverges as $1/(T)^2$. As the time to observe nucleation increases exponentially with the barrier height, then once the barrier has reached say 100 to $1000\ kT$ then the prediction is that no experimentally accessible volume of water will freeze on any experimentally accessible timescale. So classical nucleation theory suggests that a hard cutoff to nucleation at some temperature T_U may well be a good approximation.

2. A good point. There is extensive experience of fitting the GEV in other fields, and both Castillo and Jondeau *et al.* discuss this. The data in those fields is also subject to noise of course. This experience could usefully be applied here.

   I have added two paragraphs to the manuscript, to discuss fitting. The paragraphs are the last-but-two and last-but-one paragraphs in section 4.1. In the field of extreme-value statistics, plots of $\ln[\ln(1/P(T_F))]$ are sometimes used, because the sign of high T_F curvature depends on the sign of ξ. So, these plots give a straightforward way of distinguishing between the Gumbel, Fréchet and Weibull distributions. A related technique is that of Q-Q plots. I now briefly introduce Q-Q plots in the manuscript, and point out to the reader that they are discussed in my references on extreme value theory.

Grammar, minor points, etc...

1. It should. I have corrected that.
2. It is. I have reworded that sentence.