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Comment on egusphere-2022-1242

Anonymous Referee #2

Referee comment on "HUB: a method to model and extract the distribution of ice nucleation temperatures from drop-freezing experiments" by Ingrid de Almeida Ribeiro et al., EGUsphere, https://doi.org/10.5194/egusphere-2022-1242-RC2, 2023

The manuscript, “HUB: A method to model and extract the distribution of ice nucleation temperatures from drop-freezing experiments”, presents a way to simulate droplet freezing to calculate frozen fractios and ice active site density. As stated by the authors, their main goal is to link data to theory using 1 or more probability distributions. Also, they aim to described how to sufficiently sample the ice nucleation spectrum, which is interpreted as using a certain number of droplets in experiments and performing dilutions series. This will result in not too much noise in the calculated cumulative or differential ice nucleation spectra. They analyze previous data to show that a distribution of freezing events can change when solution pH changes and when cooling rate changes.

Unfortunately, I see minimal merit for publishing this study and cannot reccomend publication, unless significant revision is made. Perhaps a complete resubmission should be done. A Monte Carlo simulation to predict frozen fraction and n_s or n_m is not new and their main goals have already been accomplished by other work (Vali, 1971; Wright and Petters, 2013; Knopf and Alpert, 2013; Herbert et al., 2014; Vali, 2019; Fahy et al., 2022a; Fahy et al., 2022b). By no means is this list of references complete, the authors can look up their cited references and other studies that cite these to find numerous other models. Furthermore, the authors provide no quantitative uncertainty and no error bars, confidence intervals or prediction bands of the simulated experiments, therefore, no assessment of accuracy in this work. I did find simulating a dilution series and previous data with different pH interesting. The other new aspect is showing that the 3 probability distributions for cholesterol freezing is time dependent. For this paper to be acceptable, the authors should greatly expand their work. A resubmission should include a reproduction of other ice nucleation Monte Carlo models. To relate data and theory, they should derive a mathematical link between their model and theory as this is only discussed in a few sentences in passing despite being a main goal. Finally, they should include an uncertainty analysis of both model and experimental results, and provide new data to test their model. new data could be droplet freezing experiments and dilution series data where they know exactly what the subpopulations are before they start an experiment.

Major Comments

1) l. 18 “first available code”. This is not the first available code to predict frozen fraction or cumulative ice nucleation spectra from a probability distribution. In addition, many of other authors have made their code available, as it is a requirement for data and code availability in most journals and research grants. Therefore, this phrase or anything else similar must be removed from the manuscript.

More generally, it is likely the first time something has been done when a manuscript is published. Yes, how the authors define their probability distribution is unique, but it is distracting and unnecessary to say it is the “first time”.

l. 15-16 “no rigorous statistical analysis…to obtain a well-converged n_m that represents the underlying distribution $P_u(T)$.”. This is not true. Uncertainty are calculated by the previously mentioned studies as well, and with them one can know what is or is not in agreement, what is representative or converged or not. What the authors considers as well-converged is their opinion as there is no uncertainty estimation to claim agreement or not.

2) l. 13 “Underlying distribution” The word underlying has the meaning of something that is real or fundamental to nature. Defining probability distribution of different populations whether this is one, two or ten populations is not demonstrated here to be anything fundamental or real. “Underlying distribution” also has the meaning of something that is not immediately obvious. Whether there is one or more than one distribution (subpopulation) of freezing temperatures is always pre-defined by the authors. In other words, they authors no not derive the number of subpopulations, it is always prescribed for their forward and backward code. This is assumed not underlying.

3) Units. I cannot understand the units in Eqn 5. I know the units of n_m as Mass^{-1}, and the units of the differential spectrum N_m as Mass^{-1} Temperature^{-1}. In Eqn 5, the unit of Pmax then has to be Temperature^{-1} for the frozen fraction to be dimensionless? Would the authors include an equation of Pmax in the manuscript, and check units throughout.

4) There are no uncertainty estimate in this manuscript.

Minor Comments

1) It is common practice, that the cumulative spectra is a lower case n(T). When normalized to mass, it is n_m and when normalized to surface area it is n_s. Please change this accordingly.

2) l. 55-60 How a probability distribution connects ice nucleation experiments and theory needs to be cited and derived. This statement is unsupported. The number of freezing events defines uncertainty, and how many droplets is or is not good enough is opinion without a rigorous definition.

3) l. 70 "based on empirical bootstrapping" What was the most important in (Fahy et al., 2022a) is the non-parameteric bootstrapping was used, i.e. without any prior probability distributions needed. Here, the authors need to assume a distribution (l. 121) and already puts in bias to their methods. They have to define the number of subpopulations (l. 171), again biasing their model.

4) l. 77 The authors are not the first with a way to quantify subpopulations or different types of ice active sites or multi-component freezing to put it another way. There are too many studies to cite about mineral dust, pollen, bacteria, sea spray aerosol particles, washing water etc… A method to quantify subpopulations was done as early as 4 decades ago (Yankofsky et al., 1981).

5) l. 99 What is the difference between an underlying distribution and a true underlying distribution. Is there a false or untrue underlying distribution?

6) l. 121 Why Gaussian and why not something else? I think any distribution could be assumed. If I assumed subpopulations to exist, perhaps a Gaussian is not the best when the mean is centered on a relatively high temperature. There may be chance of sampling freezing temperatures > 0C? Of course these can be simply removed, but this would imply a bias in the subpopulation freezing behavior.

7) Too often in a section, the authors refer to later sections. Please minimize these instances, as it is distracting.

8) l. 299-301 This is circular reasoning. The authors will test the droplets and IN concentrations, to test the sensitivity of Nm to the droplets and IN concentrations?

9) l. 313 What is the authors definition of an "absolute calibration". How does this differ from a "calibration".

10) l. 374-375 What is important about looking at a log or linear scale for the y-axis of a graph. If a graph looks better or worse on either scale, what is this telling the reader? This should be clarified.

11) l. 377-379 What is the authors quantitative criteria for “almost identical” and “unnecessary”? How much data variability is explained when two, three or more subpopulations are included? Is the number of subpopulations sufficient when 99% of the variability is explained?

On the other hand, could two different types of ice nucleating particles exist (different populations) in the same drop, but have the same distribution? This code then would mistake these 2 subpopulation as a single subpopulation. This would then misrepresent the ice nucleating subpopulations?

12) l. 424-425 Here, is it assumed that pH can change the position, width and amplitude of the distributions. This is certainly important, but I am wondering how valid is the assumption that pH only changes the amplitude, but keeping the mean and standard deviation the same? As the authors prepare their resubmission and include an uncertainty analysis, I would highly recommend the authors to fit the ice nucleation data for all pH for a common mean and standard deviation, allowing only the amplitude to be a function of pH. Then evaluate if the result is somehow within the predicted and experimental error. One could surmise that a surfaces ability to nucleate ice may or may not be pH dependent, but perhaps pH would destroy active sites instead.

13) Please check references for consistency with doi format, URLs, use of italics, use of the correct journal and journal abbreviations.

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