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Comment on ”A universally applicable method of calculating confidence bands for ice nucleation spectra derived from droplet freezing experiments” by Fahy, Shalizi and Sullivan (2022).

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Abstract. Two comments are made to debate issues raised in Fahy et al. (2022)

1 Introduction

Fahy et al. (2022, F22) delves into the question of how best to derive ice nucleation spectra (spectra for short in the following) from drop freezing experiments. Among other issues, alternative data processing methods are discussed and a new method is presented for the calculation of confidence intervals. As the author of the paper that first introduced these spectra (Vali, 1971) I appreciate that F22 aims at furthering the use of the spectra. Even so, two issues raised in F22 regarding data processing and the notions underlying them deserve further comments.

2 Differential spectra derivation

The first comment addresses a relatively minor point in F22, but one that touches on the basic meaning of the spectra. Specifically, F22 (Section 2)dismiss the argument made in Vali (2019) against the use of variable bin intervals for the calculation of the differential spectrum $k(T)$. I want to reiterate here the reasons why Vali (2019) considered that approach to be problematic. Because of the widespread use of the spectra in the current literature it seems relevant to clarify the issue.

The differential spectrum is defined in Vali (1971) as

$$k(T) = -\frac{1}{X * dT} * ln(1 - \frac{dN}{N(T)}) \qquad (1)$$

where $N(T)$ is the number of drops not frozen[1] at T and dN is the number freezing within the temperature interval dT as the sample is cooled past T. The dimension of $k(T)$ is $[\mathrm{cm}^{-3}\,°\mathrm{C}^{-1}]$ for $X = V$. The use of differentials for dN and dT underscore the intention that $k(T)$ reflect nucleation activity observed at T. This is an ideal that has to be abandoned for any finite sample size (total number of drops) so that for practical use one has

[1]F22 has an error in Section 2, defining N as the number already frozen

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$$k(T) = -\frac{1}{X * \Delta T} * ln(1 - \frac{\Delta N}{N(T)}) \tag{2}$$

with the interval within which the activity is observed expanded to ΔN and ΔT. The point is that the purpose of the differential spectrum is to focus on activity at specific temperatures. The choice of the magnitude of ΔT is driven by a consideration of the interplay between desiring higher temperature resolution and the higher uncertainty resulting from smaller ΔN. In most literature the range of ΔT values is 0.2 to 1.0 °C and it is kept constant thorough the range of freezing temperatures observed in an experiment.

More discussion about about the choice of temperature interval is given in Section 4 of Vali (2019). It is argued there that using variable ΔT values, derived as

$$\Delta T = \frac{T_i - T_j}{2} - \frac{T_j - T_k}{2} \tag{3}$$

for adjacent freezing events T_i, T_j, and T_k creates a value for $k(T_j)$ that is dependent on its neighboring events. This is contrary to the intended meaning of $k(T)$.

The point made above can be elaborated with the help of an example. Fig. 1 shows a segment of the differential spectrum $k(T)$ which is shown in its totality in Fig. 4 in Vali (2019). Blue squares indicate the spectrum with $\Delta T = 0.3$°C. The heavy vertical bars in red show the same data with intervals chosen as in Eq. 3. For purposes of illustration, 6 events of the original data between -12.92^oC and -14.94^oC were removed and the spectra recalculated. The bar diagram shows the new values with $\Delta T = 0.3$°C and the dark gray circles with Eq. 3. While the bar diagram and the blue squares remain in agreement, the two dark gray points either side of the gap in freezing events show a large decrease. These are indicated by vertical arrows. The magnitude of the decrease is near a factor of 4 in both cases. The same lowering of data points near gaps in the spectrum with variable ΔT can be seen, albeit to lesser degrees, at temperatures near -16^oC, -11.4^oC and -10.7^oC.

The alteration of $k(T)$ due to changes in neighboring freezing events is an undesirable artifact. Even though the effect is minor for data with freezing events closely spaced, there is a reasonable objection to the use of variable ΔT on the basis of principle. The fixed ΔT approach treats all data points with equally across the range of observations.

3 Two perspectives

By definition, the spectra are derived from simple counting of the freezing events. Thus, the equations can be viewed as representations of the observations. Freezing temperatures of the drops are viewed as distinct events and the differential spectra represent that discreteness as best as the dats and sample size allow. Freezing events are precise temperature values (apart from instrumental errors). From the point of view of data representation that is a valid view.

In F22 the spectra are seen as inherently continuous. In Section 3.1 of F22 it is argued that given INPs and sites have site nucleation rates that can yield freezing event over the ”entire continuous temperature range”. In contrast it is argued in Vali

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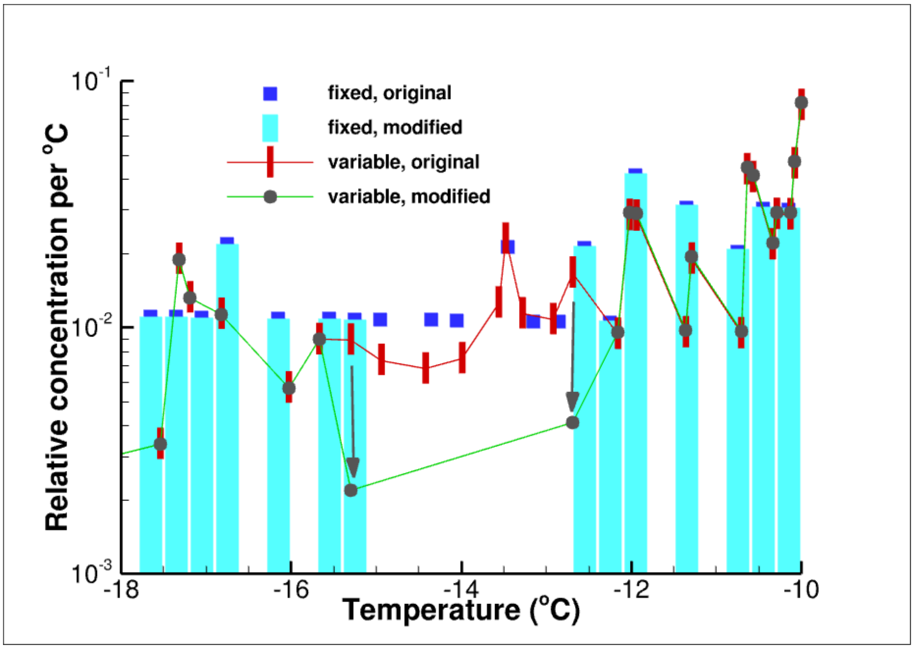

Figure 1. A segment of the differential spectrum $k(T)$ processed in four different ways. See the text for details.

(2008) that the site nucleation rate is a steeply rising function over a range of perhaps 1^oC, i.e. much smaller than the total range over which freezing events are observed for a set of drops. There is no fundamental reason for differential spectra be continuous, or even that the differential spectra be monotonically increasing. Gaps with zeroes can be indications of a real paucity of INPs active at that temperature region.

Finally, it seems evident that while parametric representations of spectra are convenient for some purposes, that is not a sufficient justification for asserting that the spectra should be always continuous in the sense just discussed.

4 Caveat

Points of the preceding paragraphs are made without consideration of the experimental precision involved in particular cases. Matching the numerical method used for calculation of the spectra will ideally be commensurate with the instrumental and sample size limitations.

The main trust of Fahy et al (2022) is a method for determining confidence limits for the nucleation spectra. Arguments in this comment against the use of variable ΔT intervals and that continuous spectra are not a rigid requirement, or consequence, of the physics of nucleation may influence that method but the connection is not explored in this Comment.

Code availability. The routines used for producing Fig. 1 were written in IDL. The code us available from the author on request.

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