Review by Markus Petters

Prof. Vali's comment concerns two claims. First, it is claimed that constant bin intervals are preferred when evaluating differential freezing spectra. Dynamic binning as proposed in Fahy et al. (2022) leads to mathematical artifacts. Second, it is claimed that there is no fundamental reason that the differential spectra are either continuous or monotonically increasing.

The comment brings to the fore a disagreement between Vali (2019) and Fahy et al. (2022) in how to compute the differential freezing spectrum. Most of the subtleties are already discussed in these preceding works. Both Vali (2019, 2023) and Fahy et al. (2022) make valid points. Also, both Vali (2019, 2023) and Fahy et al. (2022) make some claims I don't fully agree with. Ultimately, the differences between the two approaches are minor and, as argued below, the approaches are probably statistically equal once accounting for the confidence limits. Thus the approach adopted may come down to personal preference. Nevertheless, debating these issues is valuable and AMT is an appropriate forum. I therefore support publication.

Comments

First claim. Constant bin intervals are preferred when evaluating differential freezing spectra

Prof. Vali appears to be on solid statistical ground to reject dynamic binning. It is shown via the illustration in their Figure 1 that the difference is minor/negligible if the data density is high, but potentially substantial when data are sparse. To better understand the underlying arguments, I implemented both algorithms for the dataset given in Table 1 by Vali (2019), which was generated by Polen (2018). Contrary to Vali, the representation is on a linear scale to facilitate the plotting of zero values. However, Vali presents reasonable arguments to show this graph on a logarithmic scale to better visualize low k(T) values.

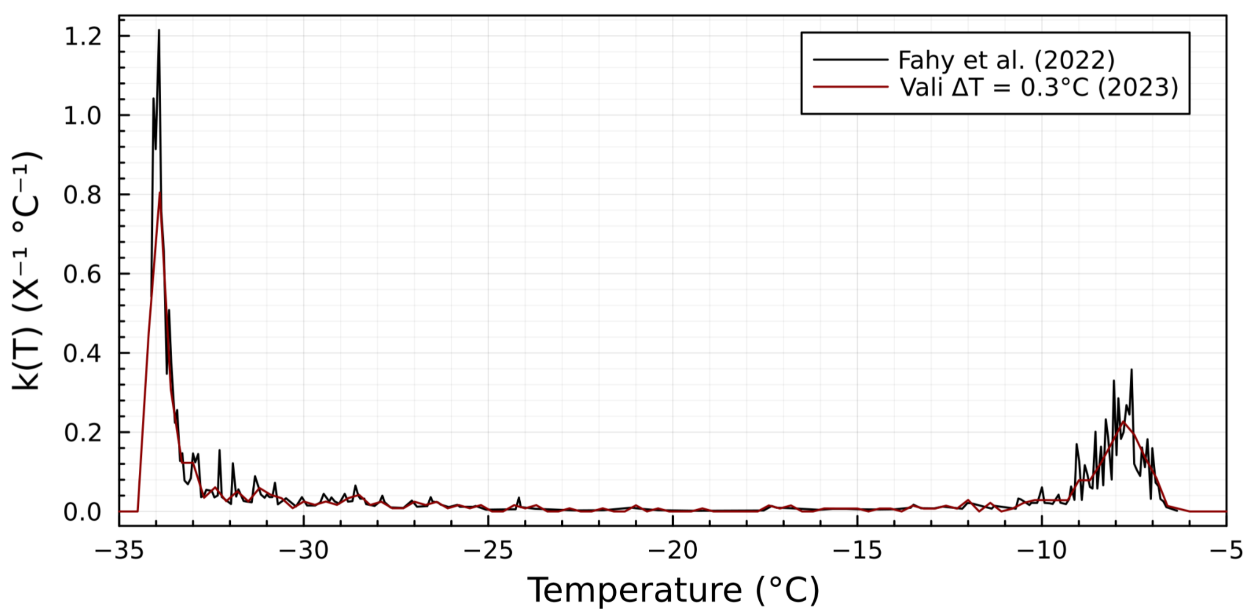

Figure 1. Comparison of k(T) evaluated using the algorithm of Fahy et al. (2022) and Vali (2019, 2023)

Comparing the difference between these implementations, my assessment of the issue is as follows.

(1) The method proposed by Fahy et al. (2022) produces a more noisy k(T). This is acknowledged in Fahy et al. (2022) and proposed to be overcome by applying a smoothing algorithm. The approach was motivated by Fahy et al. (2022) because "binning is widely accepted as an inefficient interpolation method for measurements of continuous variables such as ice nucleation activity, and has been shown to reduce statistical power and bias statistical results in data from a variety of disciplines.". Personally, I am not fully convinced that explicit smoothing is necessarily superior to the implicit smoothing provided by fixed binning. Any significant statistical bias in one or the other method would have to be proven using simulated data with known truth.

(2) The method proposed by Vali et al. (2019, 2023) with constant binning smoothes the spectra. The degree of smoothing depends on the selected bin width ΔT. Vali (2019) provides some discussion about the influence of ΔT on the spectrum and states that "it is recommended to select a suitable value for ΔT and use it for the whole data set.". However, no satisfactory rule is given for how to define suitable. Due to the uncertainty in which ΔT is optimal the method itself remains a moving target when comparing fixed binning to dynamic binning plus smoothing.

(3) The method of Fahy et al. (2022) will never yield zero k(T). As correctly argued by Vali, k(T) = 0 is a valid result that is permitted by constant binning.

(4) The method of Fahy et al. (2022) can yield artificially low results as shown in Figure 1 in Vali (2023). However, it seems to me that this is, in principle, due to the added noise that arises from effectively very narrow binning of the data. The applied smoothing algorithm may alleviate those artificially low values. Furthermore, these artificial low values are essentially due to the interpolation of no data (no freeze events) and one freeze event. The statistical confidence of these points is very low. For a fair comparison, the confidence limits should be given in Figure 1 of Vali (2023) for each data point.

(5) The broad interpretation of the freezing spectra appears to be identical whether the method of Fahy et al. (2022) or Vali (2019,2023) is used.

(6) Lastly, while the statistical details are interesting and important, one should not lose sight of the fact that the differences in the methodology is well within the expected noise of the underlying cold-stage measurements. These include temperature variability across the stage, variability in drop volume, and possible artifacts causing freezing of the drop unrelated to the INP of interest (e.g. substrate artifacts). In my opinion, cold-stage methods are not more precise than ±1 °C. Any binning that is finer than this natural limit may be of limited utility for scientific interpretation. Confidence can only be gained by observing sufficient sample size and number of independent repeats.

In summary, the difference between the two methods is small. I believe once confidence limits are applied, the methods are more or less equal from a statistical perspective. However, I agree with Vali on point (3) and in turn with his conclusion that "there is a reasonable objection to the use of variable ∆T on the basis of principle." Fixed ∆T with a broad enough bin width also obviates the need to smooth the data. What is not to like? The potential bias in the smoothing from constant binning is likely negligible, but careful statistical work might eventually show otherwise. Finally, given the real-world precision of the underlying measurements, using fixed binning using ΔT = 1.0 °C is the approach we have adopted for cumulative spectra in publications from our own group.

Second claim. There is no fundamental reason that the differential spectra are either continuous or monotonically increasing.

Vali argues that based on "Vali (2008) that the site nucleation rate is a steeply rising function over a range of perhaps 1°C, i.e. much smaller than the total range over which freezing events are observed for a set of drops.". This view is strongly supported by subsequent observations e.g. Wright et al. (2013a,b), Herbert et al. (2014), although the temperature range may be a bit wider than the claimed 1°C by Vali (2008). However, whether or not it follows from that that spectra are either continuous or not continuous is not entirely clear. It would seem to me that a given material is composed of a distribution of active sites, each with a site nucleation rate. It would further seem that the combination of a distribution of active sites of different "strength" (characteristic nucleation temperature), and some stochasticity of freezing nucleation for each active site will allow freezing to occur at any value of T. This in turn would argue for a continuous distribution. Even with a continuous distribution, the probability to encounter an active site at temperature T may be vanishingly small so that gaps with zeros in k(T) – especially for discrete sample size – are permitted under this description. I recommend removing the continuous/non-continuous discussion but the point that k(T) = 0 is a valid result stands as discussed above.

References

Fahy, W. D., C. R. Shalizi, and R. C. Sullivan: A universally applicable method of calculating confidence bands for ice nucleation spectra derived from droplet freezing experiments. Atmos. Meas. Tech., 15, 6819-6836, doi: 10.5194/amt-15-6819-2022, 2022.

Herbert, R. J., Murray, B. J., Whale, T. F., Dobbie, S. J., and Atkinson, J. D.: Representing time-dependent freezing behaviour in immersion mode ice nucleation, Atmos. Chem. Phys., 14, 8501– 8520, doi:10.5194/acp-14-8501-2014, 2014.

Polen, M., Brubaker, T., Somers, J., and Sullivan, R. C.: Cleaning up our water: reducing interferences from non-homogeneous freezing of pure water in droplet freezing assays of ice nucleating particles, Atmos. Meas. Tech., 11, 5315–5334, https://doi.org/10.5194/amt-11-5315-2018, 2018.

Wright, T. P. and Petters, M. D.: The role of time in heterogeneous freezing nucleation, J. Geophys. Res.-Atmos., 118, 3731–3743, https://doi.org/10.1002/jgrd.50365, 2013.

Wright, T. P., Petters, M. D., Hader, J. D., Morton, T., and Holder, A. L.: Minimal cooling rate dependence of ice nuclei activity in the immersion mode, J. Geophys. Res.-Atmos., 118, 1–9, doi:10.1002/jgrd.50810, 2013.

Vali, G.: Repeatability and randomness in heterogeneous freezing nucleation. Atmos. Chem. Phys., 8, 5017-5031. doi:10.5194/acp8-5017-2008, 2008

Vali, G.: Revisiting the differential freezing nucleus spectra derived from drop-freezing experiments: methods of calculation, applications, and confidence limits. Atmos. Meas. Tech., 12, 1219-1231,doi: 10.5194/amt-12-1219-2019, 2019

Vali, G.: 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), Atmos. Meas. Tech. Discuss. [preprint], https://doi.org/10.5194/amt-2023-138, in review, 2023.