# The Spread of Nucleation Temperatures of a Sample of Supercooled Liquid Is Independent of the Average Nucleation Temperature

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ABSTRACT: The stochastic nature of the nucleation of a supercooled solution is not always realized or well-defined. There exists an inherent spread of nucleation temperatures of any given sample which is repeatedly supercooled, frozen, and then thawed, in the same container, even when the nucleation is occurring at the same site. Classical nucleation theory predicts such a spread but does not provide any molecular level interpretation for the value of the spread and thus it has been the subject of some speculation. This report shows that there is a lower limit to the value of the spread which is related neither to the efficiency of the best nucleation site nor the number of times the sample is cooled and the nucleation temperature measured.
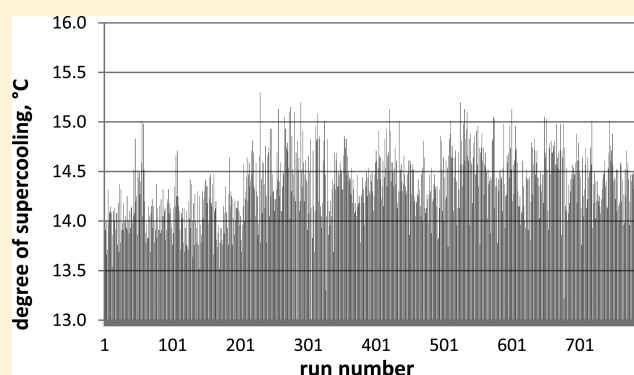
■ INTRODUCTION

Often the nucleation temperature of a liquid sample is measured by decreasing the temperature of the sample in a container, usually linearly as a function of time, until the solution freezes. This process is then repeated a few times, sometimes with the same sample but sometimes employing different samples from the stock solution. Either procedure misses one of the most important aspects of the phenomenon of supercooling, namely the inherent width of the distribution of nucleation values. When few data points are determined, the likelihood of measuring the most probable nucleation temperature is small. Haymet and co-workers have shown that at least 200−300 measurements are needed on a single sample to determine accurately the nucleation temperature.[1−4] They used an automatic lag time apparatus (ALTA), to study the statistics of liquid-to-crystal nucleation. The machine repeatedly cools, nucleates, and thaws a single, unchanging sample of solution and the setup and operation of the apparatus for aqueous solutions has been described previously.[3−7] Only a few similar examples of the protocol for determining the nucleation temperature of a supercooled liquid have been reported.[1,8,9]

This article reports an analysis of historical data, both ours and that of other researchers who have used either very similar samples, or the same sample, repeatedly cooled and thawed. We conclude that the spread of nucleation temperatures of a given sample in the same container cooled multiple times is unrelated to the efficiency of the nucleation site, and so the level of supercooling. Nor is it related to the number of times the sample is cycled through the freeze- thaw process. We are concerned here only with immersion mode freezing and our nomenclature is such that the surface of the container or particle on which the embryo of ice finally grows and crosses

the energy barrier to cause freezing is the "best" nucleation site of the most efficient site.

The spread appears to have a minimum value in the range 0.7−0.75 °C and the molecular origin for this value is not understood at this time.

■ EXPERIMENTAL METHODS

Plots from ALTA-type measurements have become to be known as Manhattans,[1−7] and give the temperature of each freezing event extended over many test cycles. A typical data set for a 200 μL volume of pure water is shown in Figure 1 where the stochastic nature of nucleation is evident. The freezing temperature of one run is independent of previous or future runs. If the stochastic nature lasts for the hundeds of cycles and there is no obvious slope or steps in the plot, then it is assumed that the sample does not change during those freeze/thaw cycles.

When data from ALTA, such as that shown in Figure 1, is analyzed further, it can produce a survival curve (a type of cumulative curve) showing the spread of freezing temperatures, as shown in Figure 2.

The temperature at which the sample has frozen 50% of the time we have called the T50 and represents the average nucleation temperature of that sample, in that container, under the specified conditions. For the data shown in Figure 2, the T50 is −14.3 °C. However, survival curves also provide natural error bars for the nucleation temperature. By measuring the 10−90 width (the range of temperature where the sample is
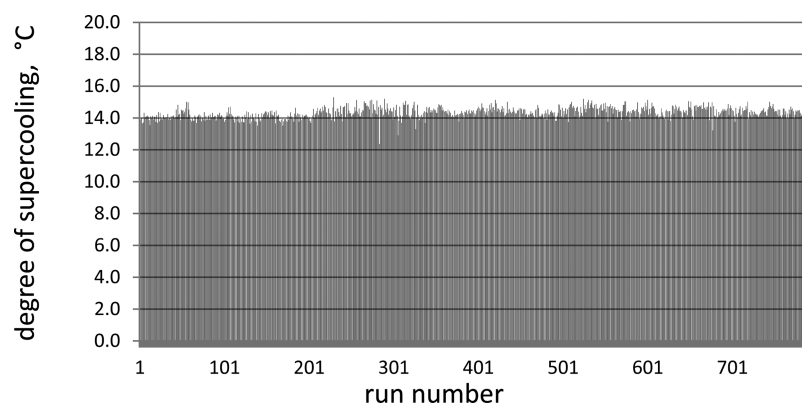
Figure 1. Plot of a typical set of 800 runs on ALTA for 200 μL of pure water, showing the stochastic nature of nucleation.[7] Each run on the same sample freezes at a different temperature and clearly there is a limited spread of temperatures also. These plots have become known as Manhattans.
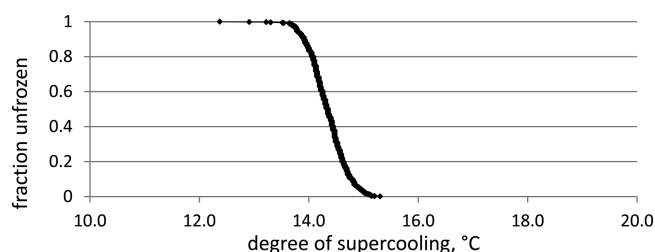

Figure 2. Nucleation survival curve for an ALTA sample set showing the spread of nucleation temperatures.[5] This data is from a 200 μL volume of water, and the raw data is shown in Figure 1. One of the most useful measures from such a curve is the 10−90 width, in this case 0.88 °C.

Table 1. Historical Data, both Ours and That of Other Workers[a]

no. of runs	sample type	volume	10−90 width, °C	T50, °C	reference
13	D	1 μL	0.73	−37.6	11
22	D	3 μL	1.0	−9.0	14
14	D	3 nl	1.12	−36.3	16
85	D	30 μL	0.81	−22.2	13
345	D	0.2 nL	1.4	−39	15
485	D	1 μL	0.7	−25	8
37211	D	0.3 nl	0.75	−37.3	10
289	D	<0.1 nl	20	−16	17
198	S	200 μL	0.9	−8.2	5
200	S	200 μL	0.73	−12.5	7
294	S	200 μL	1.75	−13	3
300	S	200 μL	1.5	−13.3	2
250	S	200 μL	1	−13	6
300	S THF	200 μL	1.4	−14.5	9
800	S	200 μL	0.88	−14.3	see text

[a]The first column is the number of runs on a given sample. In the second column D denotes different, but similar samples, and S the exact same sample run multiple times.

90% unfrozen to the temperature where the sample is 10% unfrozen), an upper and lower bounds emerge naturally from this analysis. In Figure 2 data the width is 0.88 °C. This spread in the temperature of nucleation for the exact same sample demonstrates the point that many repetitions are needed.

If two survival curves have similar slopes, and thus similar 10−90 widths, and are offset by even 1 or 2 °C then it is certain that they have different nucleation temperatures and that the stochastic nature of nucleation is not simply blurring the picture. We then have the ability to see if changes to the sample container, such as coatings, or added particles, such as crystals, can affect the T50 value. In an unchanging and clean liquid sample it is usually a defect, or some microstructure on the container wall, which is the most efficient nucleation site and initiates the nucleation and freezing process. If, however, the liquid contains a good nucleation site such as a silver iodide (AgI) crystal, a piece of insoluble dirt or sand, or even certain bacteria, then that may be the "best" nucleation site. In which case nucleation will occur at a higher temperature than it would have without the object.

■ RESULTS

We present here an assemblage of historical data, some of ours and some from other workers (see Table 1). The data is either from multiple runs on the same sample or multiple runs using what we consider to be very similar samples. Of course there exist many further data sets where different samples have been used, each with clearly different nucleators and in some cases in different containers. Such data sets have much larger 10−90 widths and are not considered further here.

Figure 3 shows 14 data points for water or aqueous solutions run at between 12 and 40,000 times. It also shows one data
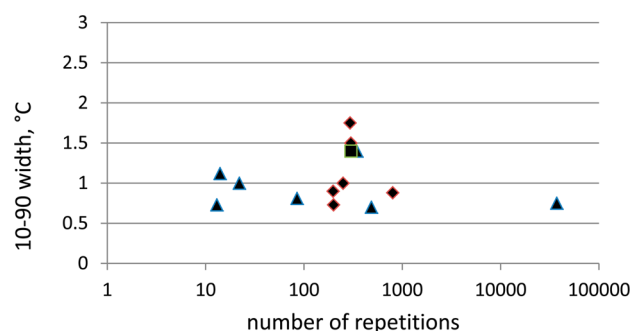

Figure 3. Collection of data from water and aqueous solutions, repeatedly frozen and thawed. Triangle data points are from measurements where the samples are similar but not identical[8,11−17] and diamonds are from the exact same sample run repeatedly.[2−7] The single square data point is a solution of tetrahydrofuran and water which solidifies as a clathrate hydrate, rather than water ice.[10] The data point at 37000 runs was produced by a microfluidics device where the droplets are very similar.[11]

point (square) for a solution of tetrahydrofuran and water which when frozen solidifies as a clathrate hydrate, rather than water ice.[10] What we see is that there regardless of the number of repetitions of freeze—thaw cycles there is a lower limit to the spread of nucleation temperatures of about 0.7 °C and the spread is typically less than 1 °C.

Figure 4 shows the same collection of data for nucleation of water and aqueous solutions as shown in Figure 3 but plotted
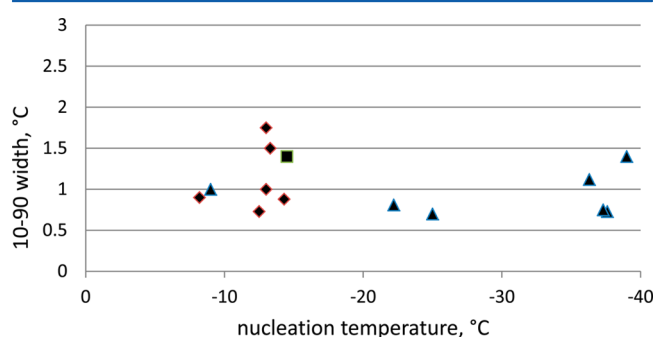

Figure 4. Collection of data for nucleation of water and aqueous solutions at various levels of undercooling. Triangle data points are from measurements where the samples are similar but not identical[8,11−17] and diamonds are from the exact same sample run repeatedly.[2−7] The single square data point is a solution of tetrahydrofuran and water which solidifies as a clathrate hydrate, rather than water ice.

as a function of the T50. It can be seen that the T50 is also not a factor in determining the 10−90 width for heterogeneous nucleation.

In Figure 4 the three data points at around −37 °C are claimed by their authors to be the result of homogeneous nucleation. The data point at 37 000 runs in Figure 3 was also at −37 °C in Figure 4 and was at, or was close to, the temperature generally accepted to be that required for homogeneous nucleation. Thus it would seem that any limit on the 10−90 width exists for homogeneously nucleated solutions also and there may be no distinction between heterogeneous and homogeneous nucleation as far as the inherent spread of nucleation temperatures is concerned. Of course homogeneous nucleation does not rely on any nucleation site, but rather is simply a fluctuation which randomly causes an "ice-like" arrangement of water molecules of critical size which nucleates and grows. There is no known molecular reason for the spread to be the same as in the case of heterogeneous, but our results indicate that the theory which adequately describes homogeneous nucleation may be closely related to whichever theory best describes heterogeneous nucleation.

■ CONCLUSIONS

From Figures 3 and 4 we have shown that there is a lower limit on the 10−90 width of about 0.7 °C. We believe this value to be inherent and unrelated to either the number of runs or to the level of supercooling. If a sample has different nucleators or even multiple nucleators within a given volume then the average spread—which is the measured quantity—will be larger.[18] In a similar way, as demonstrated clearly by Vonnegut and Baldwin,[9] the spread of nucleation times for the same sample supercooled repeatedly to a given temperature, and held, is large and certainly exemplifies the stochastic nature of

nucleation. They concluded that for every degree of super-cooling the probability of freezing increased by a factor of 4.

More recently Vali[19] has looked at ramping down the temperature for a given sample many times when there are multiple nucleation sites present. He also found that for a given sample (drop or water) the difference between freezing temperatures, i.e., the spread, was less than 1 °C. We have not included his data into Figures 3 or 4 since his data had a trend over time (ref 21, Figure 1a) between runs 1 and 55 suggesting that the nucleation sites were changing their efficiency in some way during the multiple freeze—thaw cycles. He found that the cooling rate was unimportant but did find that samples cooled more slowly tended to freeze at higher temperatures. This is, of course, reasonable since they have spent longer supercooled and had they been held at a constant temperature would have frozen at some time in the future anyway.

We now raise the question of semantics. If a drop of water has many nucleation sites deliberately introduced to it, such as soil[19] or Illite[21] then we can say that there are many sites capable of causing nucleation and that one site will be the most efficient and as the temperature is ramped down will become the (immersion mode) nucleating site at some subzero temperature which is warmer than without the additives, for the same sample of water in the same container. It is true to say however that without the additives there are many nucleation sites at the container wall, but they are simply less efficient and that one of those will be the "best" site and cause nucleation as the temperature is ramped down, albeit at a lower temperature. Indeed, if the container is very clean and smooth, or is hydrophobically coated, then it may fall to an accidentally dissolved particle of some sort within the sample to be the best nucleation site, at an even lower temperature.

Recent work by Niedermeier et al.[20] has introduced a new model for heterogeneous nucleation which is a mix of singular and stochastic-type explanations and which, when used in conjunction with droplets containing "identical" nucleators, or the same droplet measured multiple times, may well become a very useful model for heterogeneous nucleation studies. Also recently, Broadley et al.,[21] have discussed immersion mode heterogeneous freezing and outlined the differences between the singular model and the single component stochastic model. In the singular model, if the temperature is held constant but warmer than some "characteristic temperature" then freezing will not occur. In the single component stochastic model nucleation is a probabilistic, time dependent process. Broadley et al.,[21] find that in fact a multiple component stochastic model is necessary to describe their experimental data. This new model seems to explain droplet freezing experiments well and although fails with some data sets is worthy of much further scrutiny as a general model for heterogeneous freezing.

Our results show that the spread of nucleation temperatures for a given sample is in the order of 0.7 C and appears to be inherent and not an artifact of the experimental apparatus. It may now be possible to incorporate this value into theory, either CNT or some other theory. The aim of any such analysis would be to narrow down further the actual value of the surface energy of a critical embryo. For example, Murray et al.[17] use γ as the interfacial energy between ice and superooled water in their model but the value is not known with any real confidence.[22] If it could be determined with more confidence from experimental measurements, the various theories of

heterogeneous nucleation could be enhanced or altered as needed.

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Notes

The authors declare no competing financial interest.

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