

Statistics of heterogeneous nucleation of supercooled aqueous solutions in a self-assembled monolayer-coated container

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Abstract

Repeated heterogeneous nucleation of a single, unchanging aqueous sample of water in a container coated by a self-assembled monolayer (SAM) is studied using our automated lag-time apparatus showing that coating the walls of the sample container with the SAM decreases the average supercooled temperature ($\Delta T_{50\%}$) to colder temperatures, indicating that nucleation in an unmodified glass container takes place on the container walls in the absence of a substrate or impurities. Adding an AgI crystal increases $\Delta T_{50\%}$ to the same warm temperature, whether the container is SAM-coated or not, suggesting that nucleation takes place on the surface of the added crystal.

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1. Nucleation

Nucleation of a supercooled aqueous solution to form the equilibrium crystal is a simple but easily studied example of the generally poorly understood process of evolution of a metastable state to its final equilibrium state. Such processes are some of the least understood phenomena in chemistry [1,2], biology [3–6], physics [7–9] and engineering [10,11]. The lag-time before a supercooled sample nucleates to a solid is a stochastic function, strongly dependent on the degree of supercooling [12,13].

Much attention has been focused on understanding the phenomenon of liquid-to-crystal nucleation. Among the challenges is the ability to understand how to control the nucleation temperature of aqueous solutions, which is especially important when trying to understand, for example, protein crystallization. Depending upon the temperature of investigation and the aqueous solution conditions, a variety of different crystals may be

formed. The ability to grow the product of interest still remains a challenge. Control over the nucleation temperature is pertinent to other fields of engineering, including the manufacture of artificial snow and specialty foods. The data presented here, coupled with our previous work [12–14] yield a broad experimental reference set for use in both controlling the nucleation temperature and evaluating candidate theories of liquid-to-crystal nucleation.

2. Liquid-to-crystal nucleation and self-assembled monolayers

Recently, we examined the statistics of heterogeneous nucleation of a single, unchanging supercooled aqueous solution sample using a robust automated lag-time apparatus (ALTA) [13]. The apparatus used in the present experiments is identical to that described previously, and we summarize the operation here briefly. An aqueous sample of 200 μL is housed in a shortened NMR tube, which resides snugly within an aluminum block. The temperature of this block is controlled by a set of Peltiers, which control the heat flow according to the magnitude and the direction of an applied current.

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When a current is applied in a particular direction, the block and the sample are heated. When the direction of the current is reversed, the block and the sample are cooled. With this apparatus, the temperature can be decreased linearly as a function of time through a feedback mechanism, which leads to remarkably accurate control over the temperature (within ± 0.2 °C).

Fig. 1 demonstrates our success in cooling the sample linearly. The temperature as a function of time is plotted for run 75 of our pure water data set. In this work, the temperature is decreased linearly as a function of time until the sample freezes. In addition, we are able to run our apparatus in a second complimentary mode where the temperature is decreased below the equilibrium freezing temperature to a preset temperature, and the temperature is held constant until the sample freezes. A laser diode shines through the sample and onto a photodiode detector to monitor non-invasively the physical state of the sample (i.e., liquid or crystal). Interruption and scattering of the light by a newly frozen sample causes a reversal of the current to the Peltiers, and the block heats up to 10 °C for four minutes, ensuring melting of all solid micro-crystallites, before resetting the apparatus to again cool linearly for the next run. This heating and cooling cycle is then repeated a statistically significant number of times in order to accumulate the statistics of nucleation for a particular set of experimental conditions.

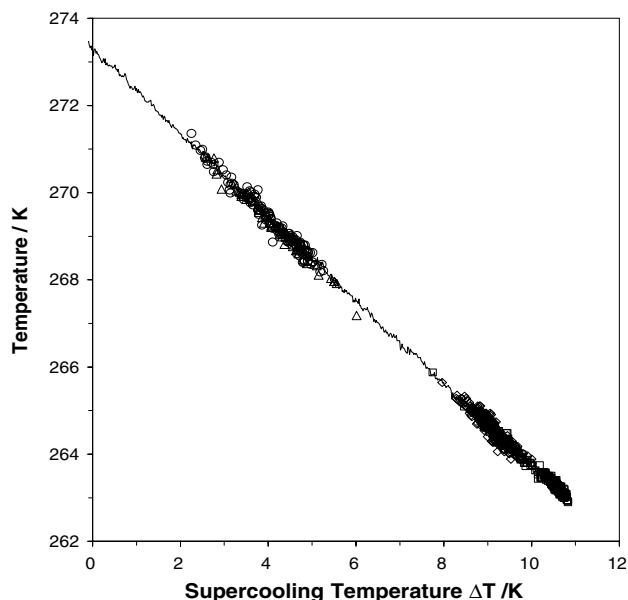


Fig. 1. ALTA raw data for the heterogeneous nucleation of a pure water sample in a SAM-coated container both with AgI seed (left circles) and without seed (right squares). The thin line is the actual recorded temperature of run 75 of the pure water experiment. Data without the SAM coating are also shown, with AgI seed (left triangles) and without seed (right diamond).

From hundreds of repetitions on a single sample, illustrated in Fig. 1, we have determined explicitly the statistical lag-time distribution, shown to be consistent with a simple, first-order kinetic model. The data are also consistent with the hypothesis that heterogeneous nucleation is occurring stochastically at moderate degrees of supercooling on an introduced, insoluble substrate when present (in our case a single AgI crystal), and at much deeper supercoolings on the walls of the sample container (probably on a scratch or crevice) when no other substrate is present. We have also investigated the accelerating effect of a gas bubble inside the supercooled liquid sample [14].

Due to the stochastic nature of nucleation, it is meaningful to report the full statistical distribution of probability and two numbers summarizing this distribution, namely, the supercooled temperature at which 50% of any ensemble of samples will be nucleated, $\Delta T_{50\%}$, and a width of the distribution encompassing the data in between 10% of the samples unfrozen and 90% of the samples unfrozen. A pure water sample containing a single insoluble crystal of AgI exhibits $\Delta T_{50\%} = 4.9$ °C. The corresponding width associated with this distribution is 3.4 °C. This width is certainly significant and physically meaningful from one data set or one set of experimental conditions to the next, but a physical interpretation to this width remains to be found. Preliminary analysis of the data we have collected thus far indicate that this width may be proportional to the efficacy of heterogeneous nucleators within our samples, namely, that a small width indicates better nucleators, while a larger width indicates weaker nucleators.

In this work, we present two new pieces of evidence to demonstrate where heterogeneous nucleation occurs within our sample cell. First, by coating the inside of our sample container, in this case a clean NMR tube, with a self-assembled monolayer (SAM; Fig. 2), we depress both the average supercooled temperature $\Delta T_{50\%}$ and the full statistical distribution to cooler temperatures, suggesting that imperfections present on the walls of the sample container prior to application of the self-assembled monolayer are partially (or perhaps even fully) 'healed' by coating the NMR sample cell with the SAM. Secondly, by introducing an insoluble AgI crystal, the average value of $\Delta T_{50\%}$ and the statistical distribution is shifted back to substantially warmer temperatures and is indistinguishable for both the uncoated and SAM-coated container, indicating that nucleation occurs predominantly (or perhaps even solely) on the surface of the crystal. It is important to note that we used the same exact AgI crystal in the uncoated container and in the SAM-coated container.

SAMs have been widely used to tailor the properties of substrate surfaces in a variety of applications [15], including the crystallization of minerals [16], amino ac-

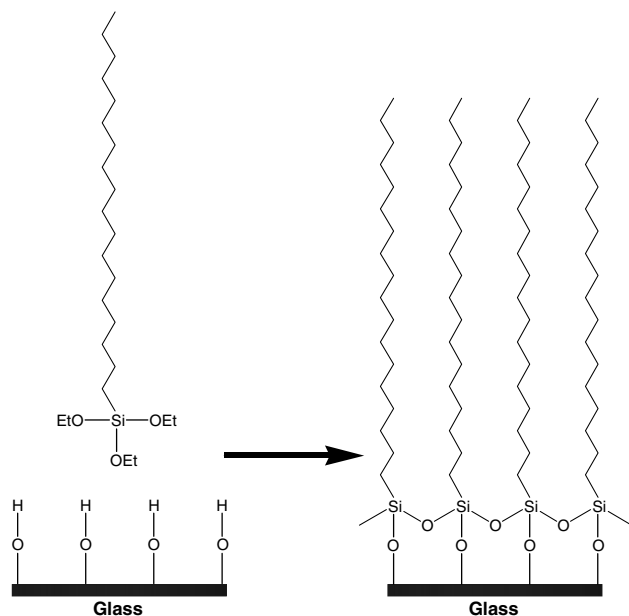


Fig. 2. Preparation of SAM-coated sample container.

ids [17], and proteins [18]. To coat the inside of the NMR tube used to hold our sample, we filled the tube with a piranha solution (a 2:1 mixture of conc. H_2SO_4 and 30% H_2O_2 solution) and let it stand for one hour. After thoroughly rinsing with distilled water and ethanol, the tube was filled with hexadecane and two drops of *n*-octadecyltriethoxysilane and allowed to stand for one hour. It was then washed with dry hexanes and allowed to dry in air. Prior to coating, data were collected for pure water and for pure water with the AgI substrate present. After coating, data were collected for the same two scenarios, leading to a consistent group of four data sets from the same sample container.

3. Results for four experimental conditions

Fig. 1 shows the data obtained from these nucleation experiments in which a single sample of pure water (200 μL) is placed in an NMR tube and cooled linearly in our ALTA below the freezing point of water until it nucleates heterogeneously. In these studies, the temperature is decreased linearly via a feedback mechanism as described above at the rate $\alpha = 1.08 \text{ K/min}$. The data collected are the lag-time τ until nucleation and the supercooled temperature ΔT at which nucleation occurs for each run, and they are plotted in Fig. 1, both for a single sample of pure water and for the same sample with a single crystal of insoluble AgI added. The thin line is the actual recorded temperature of run 75 for pure water, which shows the linearity of cooling. A total of 239 and 128 runs were collected in the SAM-coated tube

for pure water without and with the AgI crystal added, respectively. These data illustrate the stochastic nature of the observed nucleation. Elsewhere, we show that these data for pure water can be collected reproducibly over more than an order of magnitude of cooling rates [13], but here we use the slowest cooling rate from our previous work for simplicity.

In all of these experiments, we used EM Science Omni Solve reagent grade water filtered through a 0.2 micron filter. When the solution contains nucleators, either insoluble particles such as the AgI crystal utilized here, or apparent molecular nucleators such as in Antarctic fish blood and Norwegian insect haemolymph discussed elsewhere [6], the measured supercooling point is independent of which NMR tube is used. Once all of the nucleators are removed, for example in a pure water sample, we measure heterogeneous nucleation on the glass NMR tube surface. Hence, there can be a dependence of the supercooling point for aqueous samples on the particular glass surface employed. All experiments presented here used the same NMR tube, coded 20010701 in our laboratory.

We define the ‘survival probability’ as the number of samples unfrozen after time ‘ t ’, N_t , divided by the total number of samples, N_0 . The four survival curves are shown in Fig. 3 and reveal a remarkable story regarding the location of nucleation in our sample cell. The mid-points of the curves shift as described above, leading to an explanation consistent with the heterogeneous nucleation scenario described above. Furthermore, there is an inherent and reproducible width to each survival

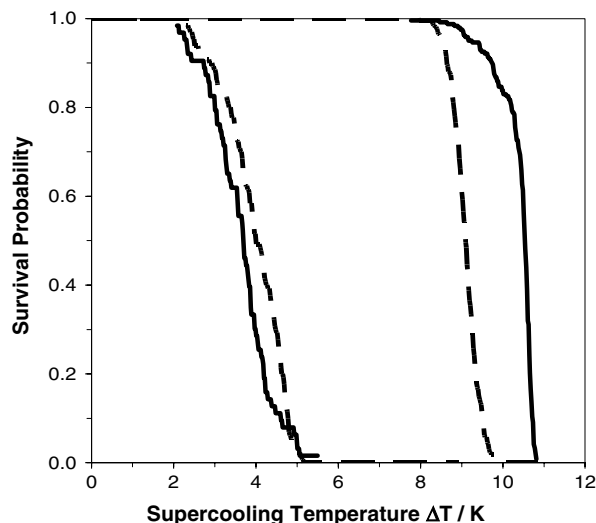


Fig. 3. Survival probability as a function of supercooling temperature for four samples of pure water in the same container under the following conditions: SAM-coated container with AgI crystal (left solid line), uncoated container with same AgI crystal (left dashed line); uncoated container, no crystal (right dashed line); SAM-coated container, no crystal (right solid line).

curve, which captures quantitatively the stochastic nature of heterogeneous nucleation [19]. Within statistical fluctuations, all four curves measured here exhibit the same width. For our linear supercooling experiment, the horizontal axis may be viewed equivalently as either the time ' t ' the sample has existed below the equilibrium freezing point or the supercooling temperature ΔT , since $\Delta T = \alpha t$. Our working definition of the so-called 'supercooling point' [13], often approximated in biological studies, is the temperature at which, on average, 50% of the samples are frozen; however, we are careful to report the width of the distribution to indicate the stochastic nature of nucleation.

4. Discussion

These results indicate that nucleation is indeed occurring on the substrate (AgI) when present in our sample cell and on the glass surface when a substrate or molecular nucleator is not present. This idea is summarized in Fig. 3, in which the survival probability remains constant when the AgI crystal is present (either in the presence or absence of the SAM), consistent with the hypothesis that nucleation is occurring at the surface of the AgI crystal and not on the wall of the NMR tube. Compare this result with the data from the run where the tube is uncoated and does not contain an AgI crystal. The probability distribution is shifted to much cooler temperatures, indicating nucleation on some other surface that is a much poorer nucleator. The hypothesis that nucleation occurs on the glass surface in the absence of substrates is further supported by comparing the results of the SAM-coated tube and the uncoated tube when there is no substrate present. When the SAM is present, the probability distribution is shifted to temperatures on average 1.4 °C cooler. The fact that we used the same tube rules out the possibility of assigning this effect to differences among individual NMR tubes. Rather, the SAM seems to 'heal' any imperfections found on the glass surface, allowing nucleation to occur (on average) at cooler temperatures. Note, however, that the midpoint of the distribution when the SAM is applied is still only -10.9 °C, which is still far from the oft-reported homogeneous nucleation temperature of -39 °C. This result indicates the need for a much more uniform container, or no container at all, before the homogeneous nucleation limit may be reached within the laboratory. Although repeated speculation exists that heterogeneous nucleation occurs at a surface such as a glass container, we believe this is the first piece of experimental evidence to support this view.

This work may be coupled with our previous work to provide a general set of guidelines for controlling the nucleation temperature. Further, this work may be

compared with our bubble-nucleation work, where we find a shift in the nucleation probability to warmer temperatures when we have a single, unchanging gas bubble formed inside the sample container. To date, we have tested only a single set of conditions for the bubble and the SAM (i.e., one bubble size and one type of film). Control of the nucleation temperature may be possible by adjusting various parameters, such as the chain length used in the SAM, and the number, size or placement of the bubble within our sample container. It is necessary to look at a variety of SAMs and bubble types (or ultimately a combination of both) to learn more about liquid-to-crystal nucleation and control of the average nucleation temperature.

Classical nucleation theory may be tested explicitly using our data in conjunction with a single, internally verifiable assumption, namely, that the survival curve decays exponentially at any fixed supercooled temperature as in first-order chemical kinetics. Over many different experiments, including the four described here, we have found this assumption to be verified explicitly [13]. Analysed in this way, our earlier survival data for pure water were shown to be many orders of magnitude away from being consistent with classical nucleation theory. In addition, classical nucleation theory predicts the size of critical nuclei to be two orders of magnitude larger than that indicated by our data. We have earlier summarized many approaches to nucleation [13], for example [10,20], and to our knowledge, there is no theory at present to explain the full range of supercooling temperatures. The rationalization of our data is in fact a test that any candidate theory of liquid-to-solid nucleation must pass.

From the very earliest considerations of the nucleation of supercooled water, which extend back to the pioneering, highly controversial, experiments of Irving Langmuir [21], who seeded clouds with AgI crystals, the question of the ultimate limit of homogeneous nucleation of pure water arises. Our experiments suggest that this limit is inaccessible in non-zero gravity due to interference from the container walls, which give rise to heterogeneous nucleation (even with SAM coatings). However, a modified version of our apparatus designed to work, for example, in the International Space Station [22], should be able to test the long-held belief that the absolute limit of supercooling of water is approximately -40 °C.

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