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Supercooling of Water

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1. Introduction

Water has a complex phase diagram with more than 16 crystalline phases, two glass phases and liquid which displays many unique behaviors, especially in the region of -45 °C (Mishima and Stanley 1998, Stokely et al. 2010). It can remain a liquid even under conditions where a more stable phase exists, and in those conditions is said to be supercooled. Supercooled water can be prompted to turn into ice by seeding, and the best seed is ice itself. The nucleation of supercooled solutions has been studied for almost 300 years beginning with the early works by Fahrenheit (see Shaw et al. 2005). Water has long been known as an unusual liquid and significant research continues today into anomalies such as the compressibility (Abascal and Vega 2011) and the fascinating tendencies when water is confined to nanoscale dimensions (Strekalova et al. 2011). High pressure density fluctuations are also an ongoing research area (Mishima 2010), as is the so-called "no man's land", a region of the phase diagram existing below the homogeneous nucleation temperature (~ -38 °C) and above where amorphous ice can be found (~ -118 °C) (Moore and Molinero 2010).

Research involving supercooled water encompasses many fields of science and atmospheric research comprises a large fraction of these works (DeMott 1990, 1995). Ice formation in the atmosphere affects rainfall and snowfall as well as the level of solar radiation reaching the Earth's surface and so is very topical of late (Sastry 2005, Hegg and Baker 2009). In clouds, supercooled water droplets are thought to sometimes freeze homogeneously through the organization of water molecules into an ice lattice without the need for any external seeding agent (Tabazadeh et al. 2002, Ansmann et al. 2005). Picolitre volumes of liquid water can be cooled in the laboratory to about –39 °C before freezing occurs and this homogeneous nucleation temperature is usually denoted as T_{homo} or T_{hom} (Koop and Zobrist 2009, Stan et al. 2009).

In biological systems some plant cells adapt to subfreezing temperatures by deep supercooling, with temperatures as low as –60 °C reported (Kasuga et al. 2007, 2010). In the case of insects it has been shown that most have the ability to supercool in the absence of gut content, but this does not automatically mean that they cold-hardy (Bale and Hayward 2010, Doucet et al. 2009). Supercooling to –40 °C has been reported in some freeze-avoiding, cold-hardy insects (Sformo et al. 2011). Conversely freeze tolerant insects, such as the New Zealand alpine weta, avoid supercooling by causing ice to form at high sub-melting point temperatures (Wharton 2011).

The addition of solutes to water causes a depression of T_{hom} (Koop 2004) but in contrast the addition of ice nucleating agents (INAs) raises T_{hom}, and as we will see later also T_{het}, the heterogeneous nucleation temperature.

The usage, or avoidance, of supercooled water can be important in industry. For instance, thermal storage air conditioning systems use water as a phase change material and supercooling is a serious problem. Controlling the phenomenon is highly advantageous (see for instance Chen et al. 1999).

Since supercooled water is a metastable state, most studies on supercooled water actually are concerned with the liquid to solid transition (Langham and Mason 1958). In order to describe the liquid to solid transition mathematically Classical Nucleation Theory (CNT) was formulated by Frenkel and others in the 1930s. The history of CNT is outlined in a thorough review by Kathmann (2006).

Concerning nomenclature, the temperature at which a solution spontaneously freezes when cooled below its equilibrium freezing temperature, T_f, is denoted variously as the "kinetic freezing point" (MacKenzie, 1977), the "temperature of crystallization" (Vali 1985) and the "nucleation temperature" (Kristiansen et al. 1999), regardless of whether it is T_{hom} or T_{het}. For biological solutions, or even for whole organisms, this temperature of spontaneous freezing is also often called the "supercooling point" (SCP) (Zachariassen 1985) and this is the notation adopted in this article.

2. Homogeneous nucleation of supercooled water

The homogeneous nucleation temperature T_{hom} of liquid water is generally accepted to be approximately -39 °C. Below this temperature even finely dispersed water droplets will freeze instantly. It has also been proposed that this temperature is somewhat volume dependent and this concept, together with the reported anomalous density data of supercooled water, are discussed by Hare and Sorensen (1987). A brief review of the homogeneous nucleation of liquids can also be found in Debenedetti and Stanley (2003).

In practice, the phenomenon of homogeneous nucleation is actually very difficult to achieve under laboratory conditions. In order to approach the limit of homogeneous nucleation, much care must be taken in the preparation of the sample to avoid impurities, which may lead to heterogeneous nucleation. One method to achieve homogeneous nucleation takes advantage of extremely small volumes of ultra-pure water, which are immersed within oil emulsions (Broto and Clausse 1976). As the sample volume becomes smaller, there is a greater probability that impurities are absent from the liquid droplet. The oil acts to prevent extra surfaces or sites on which the sample may nucleate. A second method to achieve homogeneous nucleation involves levitating a small volume of aqueous solution by using an electromagnetic field (Kramer et al. 1999). Although this elegant method eliminates the use of a container, which again may introduce unwanted sites for nucleation, it does not ensure a sample free of impurities. Hence, most, if not all, nucleation encountered in the laboratory and in practical experience is heterogeneous. Even nucleation of clouds in the atmosphere is now believed by some to occur entirely or mostly on a seed particle such as ammonium sulfate (Hung et al. 2003).

Since any supercooled biological system is not actually composed of ultra-pure water, the effect of solutes on the SCP must be addressed, even though solute-induced decrease of T_{hom} is somewhat difficult to measure. Rasmussen and McKenzie (1972) reported the T_{hom} for a variety of aqueous solutions of increasing concentration, and their data suggested that T_{hom} decreased by about twice the equivalent melting point depression, for a given volume and measurement technique. This ratio is usually denoted λ. More recently, Koop et al. (2000) analyzed the reported T_{hom} of 18 different solutes as a function of solute molarity. In essence their work showed the ratio is unity for all physiological strengths, and that the identity of solute species is unimportant. Miyata et al. (2002) argue that there exists a strong correlation between T_{hom} and ionic radius of alkali ions and/or halide ions. They argue that some of the results of Koop et al. were at best an approximation, at least in the case of ions. Koop et al. (2004) subsequently wrote a more thorough review where they also discuss some desirable future experiments.

In another review Zachariassen and Kristiansen (2000) discuss homogeneous nucleation, and argue that it may actually be the mechanism of freezing in some biological systems. They contend that nucleation in some insect species is not triggered by ice nucleation agents of any sort and that they instead undergo homogeneous nucleation. Wilson et al. (2003) found their argument flawed due to its reliance on the interpretation of the results of Bigg (1953). The "homogeneous" nucleation results of Bigg were brought into question by Langham and Mason (1958) from the same laboratory a few years later, and it seems that the results of Bigg have never been reproduced. The high T_{hom} values reported by Bigg are possibly due to some heterogeneous process involving a reaction at the water-oil-surfactant interface.

3. Heterogeneous nucleation of supercooled water

Heterogeneous nucleation and reports surrounding it have been reviewed by Sear (2007) who points out that if we concede to having a meager understanding of homogeneous nucleation then our understanding of heterogeneous is even worse. Heterogeneous freezing, where the freezing event is initiated on a foreign surface, particle or even molecule, has been hypothesized to occur in four different ways: deposition nucleation (Dymarska et al. 2006, Kanji and Abbatt 2006, Kanji et al. 2008, Mohler et al. 2006); condensation freezing (Diehl et al. 201); immersion freezing (Marcolli et al. 2007) and contact freezing (Cooper 1974, Durant and Shaw 2005, Fukuta 1975a,b, Pruppacher and Klett 1997, Fornea et al. 2009). This range of freezing mechanisms makes experimental determination of T_{het} problematic. For instance, it has been found that freezing seems to occur at higher temperatures in contact mode than immersion mode (Pruppacher and Klett 1997). Similarly it has been suggested that even with homogeneous nucleation the initial event is occurring at the water surface as opposed to within the bulk (Tabazedah et al. 2002) and evidence for this has also been provided by Shaw et al. (2005).

Apart from ultra-pure water sequestered in emulsions to reduce the contact with solid surfaces, all other aqueous solutions will undergo heterogeneous nucleation (Fletcher 1969). The liquid sample must be housed in a container of some form and even so-called "pure" water will, in general, have some impurities about which nucleation might proceed. From a free energy point of view, it is more favorable to grow an ice embryo on a two-dimensional surface than in a three-dimensional surface-free volume of water (Duft and Leisner 2004, Sigurbjornsson and Signorell 2008).

When the volumes of water used in an experiment are larger than the micron-sized droplets found in emulsions, and they are supercooled, T_{het} varies markedly due to varying amounts of impurity particles, which may act as sites where nucleation may occur. Hosler and Hosler (1955) used a variety of sizes of capillary tubes and found that, even when the capillaries had an diameter of only 0.2 mm, the lowest temperature they could reach with water samples was –33 °C, at which point heterogeneous nucleation occurred. Most workers who use differential scanning calorimeters (DSC) use water as a control at one time or another. These workers usually find that the typical sample volume comprised of only 5 µl of pure water will invariably freeze in the DSC pan at temperatures ranging between about –21 °C and –25 °C (Wilson et al. 1999), which is far from T_{hom}.

With slightly larger volumes, studies have shown that 200 µL of clean, reagent grade distilled water sealed in a glass NMR tube typically freezes at temperatures around –14 °C, and that this temperature is somewhat container dependent when there is no efficient nucleator present in the aqueous sample (Heneghan et al. 2002). Using even larger volumes tends to make it more difficult to achieve low nucleation temperatures, simply because it enhances the probability of the presence of an efficient nucleator. Dorsey (1948) published a very thorough study cleanliness, glass type, and the effects of water conductivity on the heterogeneous nucleation temperature of water. Sample sizes of approximately 4 mL were used and at no time was he able to cool the water below about –19 °C before heterogeneous nucleation occurred. Inada et al. (2001) have managed to supercool several hundred mL of water down to temperatures around -12 °C, a major achievement for such a large volume of water.

4. Measuring the supercooling point

The stochastic nature of the value of T_{het} is not always realized or well defined historically (Barlow and Haymet 1995, Heneghan et al. 2001). Often the SCP is measured by sealing the solution into a small capillary, and decreasing the temperature of the capillary linearly as a function of time at some preset rate until the solution freezes. This process is then usually only repeated a few times, employing different samples from the stock solution in each successive run. This procedure misses one of the most important aspects of this phenomenon, namely the inherent width of the distribution of SCP values (Vali 2008, Wharton et al. 2004). In the case of whole animals, the procedure is essentially the same, but great care is taken to ensure that the animal is not seeded with ice, which would prematurely induce freezing in supercooled fluids (Ramlov 2000). In this method, the lowest temperature reached prior to the sample freezing is defined as the SCP of the solution. Freeze-tolerant animals may survive the experience, and the same sample may be used several times to investigate the natural width of this supercooling point temperature, but not so with freeze avoiding animals.

Quite often, SCP determinations have been made from only a handful of measurements on each sample, or on each stock solution or on each group of animals, and the resulting values quoted with standard a deviations calculated in the usual way. However, if so few data points are determined, the likelihood of measuring the most probable nucleation temperature is small. In fact, Haymet and co-workers have shown that up to 200-300 measurements are needed on a single sample to determine accurately the nucleation temperature. They use an automatic lag time apparatus (ALTA), to study the statistics of

liquid-to-crystal nucleation (Heneghan et al. 2004, Barlow and Haymet 1995). The machine repeatedly cools, nucleates and thaws a single, unchanging sample of solution. It operates in a linear cooling mode, in which the temperature of a single sample of liquid is decreased by a constant rate until the sample freezes. The set-up and operation of the apparatus for inorganic aqueous solutions has been described in Heneghan et al. (2002), Wilson et al. (2003, 2009, 2010), Wilson and Haymet (2009). Other workers are now using a similar analysis (see for example Seeley et al. 1999).

A typical data set from ALTA is shown here. Known as a Manhattan, it gives the time each run spends supercooled, and since cooling is linear this is also the temperature of each freezing event.
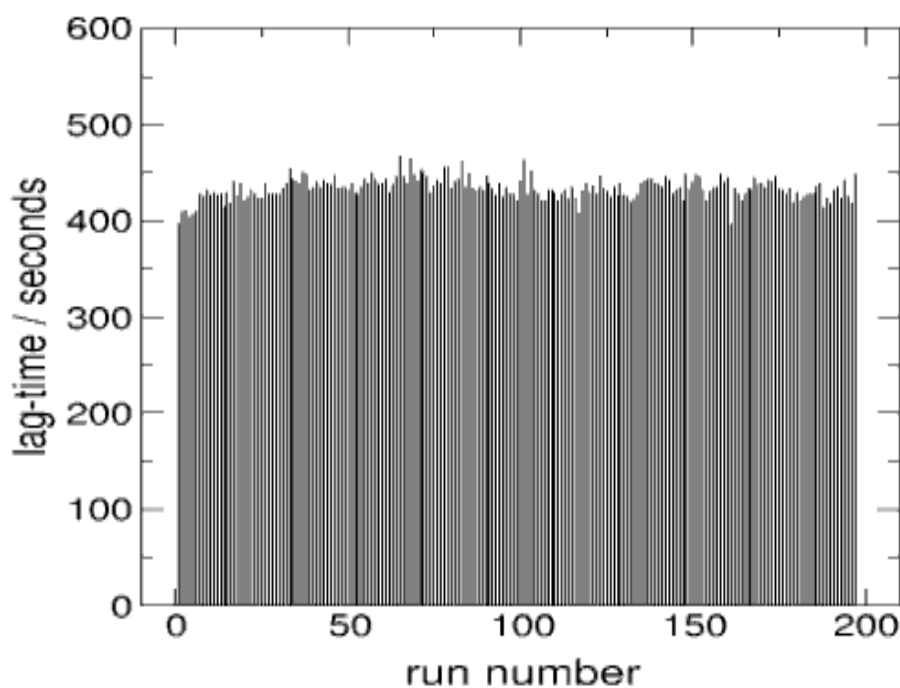

Fig. 1. Manhattan for a typical set of runs on ALTA, showing the stochastic nature of nucleation, where each run on the same sample freezes at a different temperature.

When data from ALTA is analyzed further it can produce a survival curve, a type of cumulative curve, showing the spread of freezing temperatures, as shown in fig 2.

The curves shown in Figure 3 show nucleation of the same single water sample in the same tube both with, and without, a crystal of silver iodide added to lower the free energy barrier. The SCP is then defined as the 50 % height of the survival curves, and has been shifted warmer by 7.7 C with the addition of the silver iodide.

Classical nucleation theory (CNT) was developed to describe the vapor to liquid transition (see for example Auer and Frenkel 2001) and is generally not appropriate for the liquid to solid transition. Results from ALTA experiments with pure water and water with an added catalyst have shown that CNT produces values incorrect by many orders of magnitude (Heneghan et al. 2001). The ALTA results show that the size of the critical ice nucleus needed to initiate the phase transition is much smaller than CNT predicts. Also, these
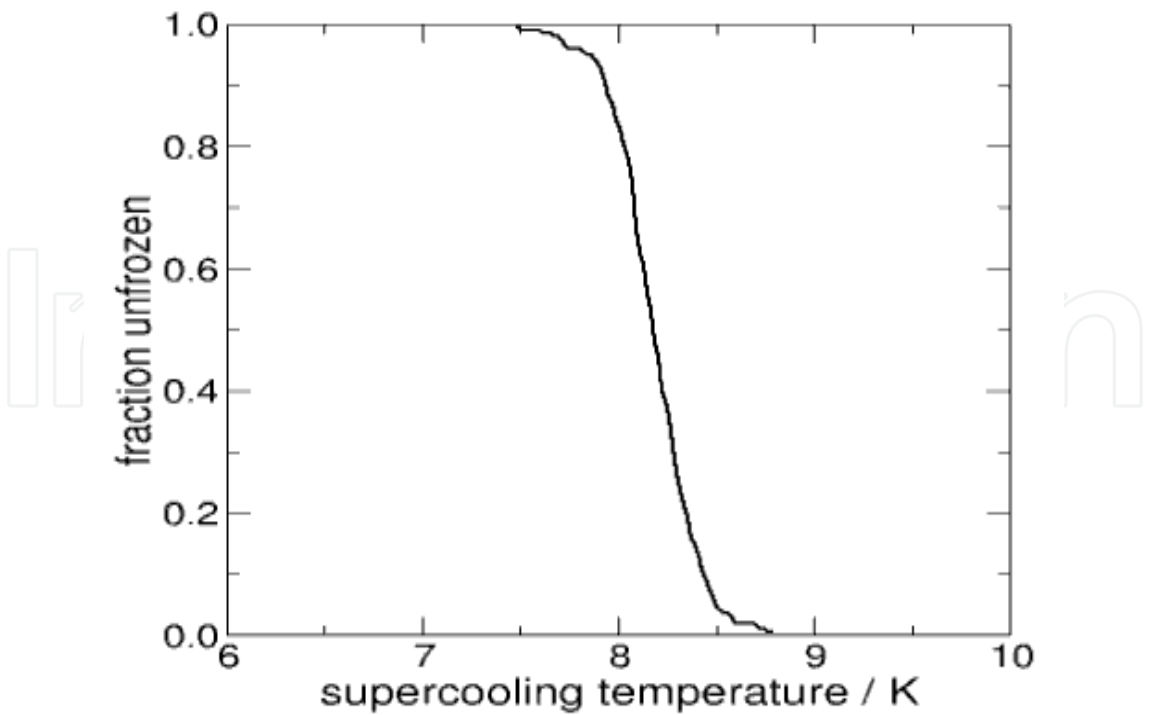
Fig. 2. Nucleation survival curve for an ALTA sample set showing the spread of nucleation temperatures. One of the most useful measures from such a curve is the 10-90 width, in this case about 0.7 °C.
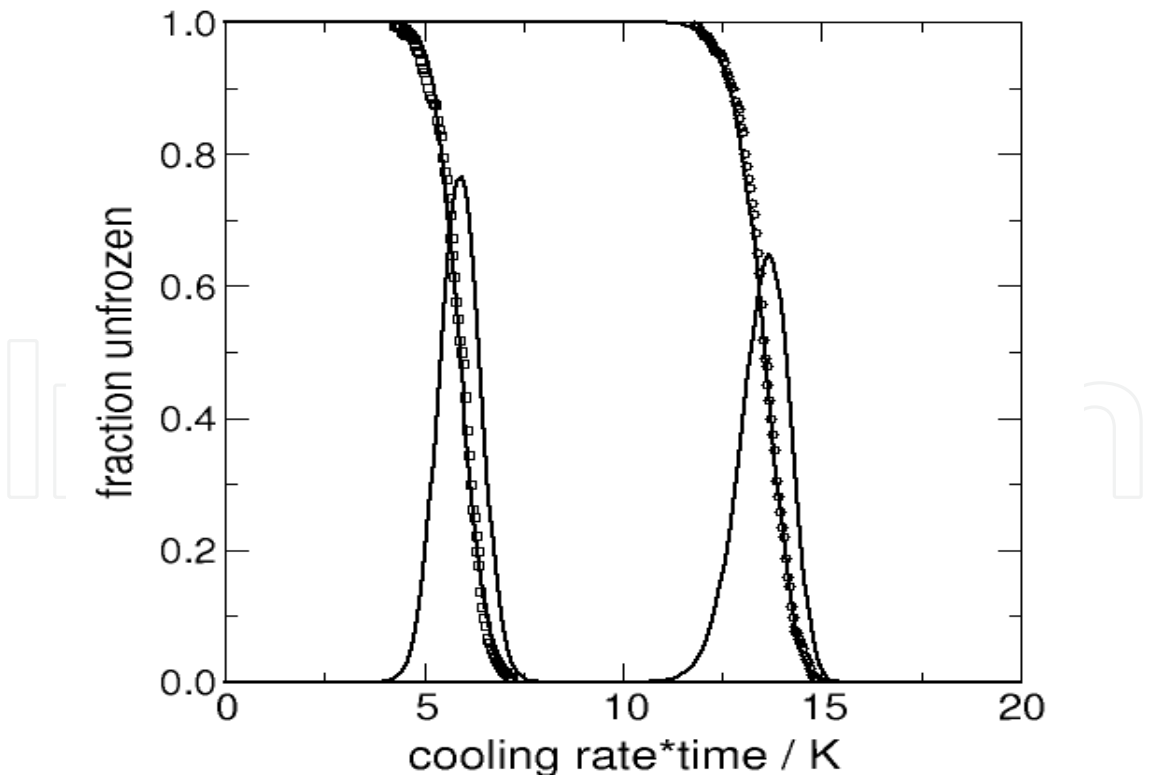

Fig. 3. If the first derivative of the survival curves (Fig. 2) is taken the resulting peaks show the probability of nucleation as a function of temperature. The 10-90 width is almost exactly the same as the full width at half height of these peaks.

experimental results are in agreement with recent theoretical calculations of Oxtoby who has used density functional theory to show that CNT is overly simplistic (see for example Shen and Oxtoby 1996).

The natural definition of the SCP is the temperature at which the survival curve crosses the 50 % unfrozen mark, namely the temperature at which on average half of the samples are frozen and half of the samples are unfrozen. For the data shown in Fig. 2, the proposed SCP is 8.17 K below the melting point. However, this survival curve also provides natural error bars for the SCP. By measuring the 10-90 width (the range of temperature where the sample is 90% unfrozen to the temperature where the sample is 10% unfrozen), an upper and lower bounds emerge naturally from this analysis. Here the 10-90 width is 0.7 K. This large spread in the temperature of nucleation for the exact same sample demonstrates further the point that many repetitions are needed. In other experiments utilizing droplets with volumes of 1 µl, some 500 to 600 thermal cycles have produced a 10-90 width of 0.75 C (Seeley et al. 1999).

5. Effect of electric field on supercooled water and nucleation

The ability to promote or suppress nucleation would have profound impacts on many fields such as cryopreservation, prevention of freezing of crops, cloud seeding, snow making to name but a few. One possibility for such manipulation might be the addition of an electric field. The effects of an electric field however are still under debate. Wilson et al. (2009) could find no effect on T_{het} for DC fields up to 10^5 Vm^{-1}, and similarly Stan et al. (2011) found no effect on T_{hom} for fields up to $1.6*10^5$ Vm^{-1}. In contrast, Wei et al. (2008) found that fields of up to $1*10^5$ V/m could affect the SCP, albeit by only 1.6 °C. It cannot be ruled out that the inherent stochastic spread of T_{het} would show such a spread in any event. In another study Ehre et al. (2010) found that water freezes differently in positively and negatively charged surfaces of pyroelectric materials.

6. Effects of solutes on the nucleation of supercooled water

With regards the SCP one important question is whether, for a given solution and container, added solutes actually decrease T_{het} by an amount which is the same as the melting point (m.p.) depression, or twice as much, or three times? Even this seemingly simple measurement has proved somewhat problematic. Koop et al. (2000) claim that the identity of the solute species has no effect whatsoever on the ratio of the SCP depression to the m.p. depression. In a similar way the correlation between ionic radius and the SCP ratio has also been studied (Miyata et al. 2002). Block and Young (1979) reported that added glycerol decreases T_{het} of some particular solutions by more than three times the equivalent melting point depression. Wang and Haymet (1998) have shown that even within the simple sugars, the amount of supercooling decrease for a given volume differs from one isomer to another. They found that trehalose and sucrose decreased T_{het} in a modulated DSC further than glucose and fructose.

This ratio, λ, has also been examined closely by Duman et al. (1995) and λ has been found to vary from unity to about two by Block (1991). It has been argued theoretically that λ should

be unity, even for homogeneous nucleation (Franks, 1981). In whole animal studies on species lacking ice nucleating agents, λ has been reported to be closer to three (Somme 1967). In contrast, in all other studies where potent nucleators are present, λ has been reported to have a value very close to unity (Lee, 1981). Zachariassen (1985) found that adding either saline or gylcerol at concentrations up to 2.5 osm. increased the SCP (same volume, same container) by a factor between 1.4 and 1.5. More recently Zachariassen and Kristiansen (2000) contended that the polyol accumulation in freeze-tolerant insects generally only decreases the SCP by a ratio of unity.

In the case of T_{hom} Kanno et al. (2004) found that λ is affected by the nature of the solute, contrary to the conclusion of Koop et al. (2000) and is close to 2. Kimizuka et al. (2008) found that λ depends on the molecular weight of the species, for PEG, PVP and dextran, and values vary between 1.5 and 4.5. They also found that values correlate with the log of the self diffusion constant. Takehana et al. (2011) found that aqueous solutions of H_2SO_4 did not follow the linear relationship and that λ was in fact a quadratic relationship with molarity.

It is clear that to measure accurately the nucleation temperature, many more measurements are needed than have typically been made in experiments published to date. Also, the solute dilution series must be carried out in the same container and under the same conditions, such as rate of cooling. Wilson and Haymet (2009) have investigated the effect of solute concentration on T_{het} of aqueous solutions of both NaCl and D-glucose. Using the ALTA technique allowed the dependence of T_{het} on solute concentration to be determined with statistical significance. The results showed that the solute-induced lowering of T_{het} was in fact λ=2, at any fixed concentration, the same factor reported for homogeneous nucleation experiments with small molecular weight solutes.

7. Theories of nucleation

The tool used most often in modeling studies of liquid to solid nucleation is CNT. This theory uses the capillarity approximation whereby the properties of the critical cluster (and smaller) are considered equal to those of the bulk new phase. This approximation is questionable when the number of molecules making up the cluster is perhaps a few hundred to a few thousand. A clear description of the shortcomings of CNT can be found in Erdemir et al. (2009) who advocate a two-step model for nucleation of solids. A thorough review of theories of nucleation has been given by Hegg and Baker (2009), who also provide an overview of the state of the art with regard to theories of nucleation in the atmosphere.

Statistical mechanics has also been used to develop another theory of nucleation of this phase transition, the inadequacies of which are reviewed in Ford (2004). Classical density function theory (DFT) (Granasy 1999) has been recently used to look at heterogeneous crystal nucleation (Kahl and Lowen 2009) who describe it as an ideal tool to look at this problem. In contrast, for deep quenches spinodal nucleation theory is said to be needed (Wang and Gould 2007) who modeled the homogeneous and heterogeneous nucleation of Lennard Jones liquids. The concept of cluster chemical physics and associated dynamical nucleation theory (DNT) is discussed by Kathmann (2006). He has been able to do little

more than point out the inadequacies however, since the constants used in the models are not currently known with sufficient accuracy. A look at CNT and quantum nucleation theory as it pertains to liquid to gas nucleation can be found in Maris (2006).

8. Supercooling in biological systems

The supercooling abilities, and otherwise, of some insect classes is reviewed by Doucet et al. (2009). Current climate change and the effects on cold-hardy insects has been discussed by Bale and Hayward (2010) who also include a brief overview of the supercooling abilities of over-wintering insects. The supercooling abilities of some plants, including trees, are discussed in Kasuga et al. (2007) and a general overview of nucleation and anti-nucleation in biological systems is given by Zachariassen and Kristiansen (2000).

The special case of ice-binding proteins and the effects on T_{het} is examined more closely now. These special classes of proteins are often called antifreeze proteins (AFPs) and are thought to bind to ice to stop macroscopic growth inside many organisms. However, it is their effect on supercooled solutions which is of interest here.

Some of the body fluids of polar fishes, such as the eye, are supercooled for the duration of the life of the fish, albeit by less than 1°C. The gut contents are not supercooled since ice crystals will almost certainly be present as the fish swallow sea water. In the large Antarctic toothfish *Dissostichus mawsoni* there may be as much as one liter of blood, and if no ice were ever to enter through wounds or the gill filaments this may be supercooled for as long as 50 years. Even at 1 °C of supercooling such fluids still have the chance of heterogeneously nucleating ice and the presence of AFPs would then be necessary. It is still unclear whether one purpose of AFPs in polar fishes is to inhibit nucleation in the blood, since ice crystals are in fact present in the gut, and at times in the blood. Clearly the main job of AFPs is to inhibit the growth of crystals already present in environments conducive to growth.

Many insects/arthropods deliberately choose supercooling as a freeze-avoiding strategy and they too have AFPs in their haemolymph. In these cases the question remains as to whether the AFPs inhibit the nucleation of ice.

Conversely, biological ice nucleation has also been the focus of much research, especially in relation to plants and crop protection (Levin and Yankofsky 1983). It is well known that some bacteria produce very effective ice nucleation proteins (INPs) to enhance nucleation of ice at very high subzero temperatures. This topic is reviewed in Burke and Lindow (1990) who modeled these large proteins and assigned sizes and nucleation temperatures for particular scenarios. Since AFP molecules are thought to bind to ice to stop growth it is a small step to study larger proteins which bind water molecules to themselves in order to make a large enough "ice crystal" to pass the Gibbs free energy barrier and cause the solidification event. There have been sporadic reports of solutions with AFP being able to supercool further than workers would have expected, however, as we have seen there are inherent difficulties in measuring accurately the SCP. Duman (2002) has produced some interesting results with citrate. Basically, he found that AFPs from the beetle *Dendroides*, together with glycerol or citrate, can eliminate the activity of potent ice nucleators and thus lower the SCP further than without the added citrate. This concept seems not to have been

explained fully to date. In contrast, Larese et al. (1996) found that adding AFP type I to animal cell suspensions actually increased the incidence of intracellular ice formation. The explanation being that the AFPs bound water to themselves and helped the embryonic crystal grow to sufficient size to cross the energy barrier.

The question arising from the work on AFPs and supercooling is as follows: Do AFPs find embryonic ice crystals and bind to them and stop them becoming large enough to cross the free energy barrier or do they bind to the most likely site of ice nucleation and mask it from water molecules, thus lessening the probability of nucleation? Wilson and Leader (1995) argued for the latter. Before any further insight can be gained into the effect of AFPs on nucleation it is necessary to be able to measure the supercooling point much more accurately in biological systems than has perhaps been generally possible to date. Holt (2003a,b) showed that antifreeze glycopeptides (AFGP) at 1% concentration could significantly lower the SCP when diluted with tap water. However when there was a strong nucleator present the SCP increased, and he put this down to the AFP joining the nucleators together, although there appeared to be no real evidence for that.

In a recent study Wilson et al (2009) examined the effects that antifreeze proteins have on the supercooling and ice-nucleating abilities of aqueous solutions. Using the ALTA technique, they showed several dilution series of Type I antifreeze proteins. Results indicated that, above a concentration of ~8 mg/ml, ice nucleation is enhanced rather than hindered. They went on to present a new hypothesis outlining three components of polar fish blood that which they believe affect its solution properties in certain situations.

9. Conclusion

All nucleation of supercooled biological solutions or whole animals is heterogeneous and this is probably true for most non-biological solutions as well. Many repetitions on the same or "identical" samples are required to measure accurately the SCP, and its partner quantity, the inherent width of the survival curve. Also, solutes decrease the SCP of solutions by twice as much as the equivalent melting point depression.

10. Acknowledgement

11. References

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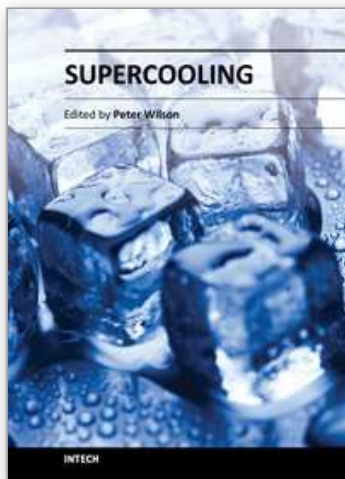
Supercooling

Edited by Prof. Peter Wilson

Supercooled liquids are found in the atmosphere, in cold hardy organisms, in metallurgy, and in many industrial systems today. Stabilizing the metastable, supercooled state, or encouraging the associated process of nucleation have both been the subject of scientific interest for several hundred years. This book is an invaluable starting point for researchers interested in the supercooling of water and aqueous solutions in biology and industry. The book also deals with modeling and the formation subsequent dendritic growth of supercooled solutions, as well as glass transitions and interface stability.

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