RATE OF ICE FORMATION IN SUPERCOOLED WATER

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In this paper we argue that the form of the crystallisation curves obtained for supercooled water and benzene can be explained by assuming a two-step process. This hypothesis can also give a phenomenological explanation of the behaviour of a system subject to precooling, as well as the rate dependence on the crystallisation. We predict how the onset time will depend on the duration of the precooling. We give a number of arguments to support the idea of an intermediate phase. The description does not rely on small fluctuations in order to trigger the crystallisation process.

1. Introduction

This paper is an attempt to explain the crystallization rates observed when using various cooling methods. In particular we are describing the influence of precooling, i.e. supercooled liquids that are subjected to a two-step process: first kept at an extra low temperature and then at a moderately low temperature, both below the freezing point.

The first part of the paper is concerned with the shape of the crystallisation curve of liquids that are kept at a constant supercooled temperature. The rate of ice formation, as originally proposed by Biggs [1] leads to an exponential increase of the amount of ice and this seems to contradict the experiments of Broto and Clausse [2]. These authors observe that the initial slope of the crystallisation curve is approximately zero, in contrast to the finite slope given by the Biggs equation. This result was confirmed in experiments on benzene [3]. The observation of the small initial rate, leads us to suggest that the process of spontaneous crystallisation is really a two-step process in which an intermediate substance is formed first. This hypothesis is worked out in section 3.

In addition, this new scheme can be used to provide a description of the precooling experiment of Clausse and Broto [4]. In these experiments the supercooled liquid is not immediately maintained at the final temperature $T_2$, but is first kept at $T_1 < T_2$ for a given length of time. This cycle leads to an enhanced crystallisation probability. Another way to express this is to introduce the concept of onset time or incubation time. The experiment shows that this incubation time is shortened if the liquid is pre-cooled.

Finally we work out the influence of the cooling rate on the probability of crystallisation. Using a simple functional form for the temperature dependence of the rate of ice formation, we show that if the final temperature is reached at a slower pace, more of the intermediate substance is formed and the probability of crystallisation is enhanced in accordance with observation.

2. The role of rate equations in the ice-forming process

The simplest description is to assume that in each volume element of water there is a constant attempt to make crystal-embryos. Only a fraction
of these embryos will grow to the required critical size to form a germ. (A germ leads to the ultimate crystallisation process, whereas an embryo might disappear after its formation.) Hence the probability to start ice formation is proportional to the volume of water

\[ \frac{dn}{dt} = k(n_x - n), \]  

(1)

where \( n \) is the amount of ice, \( n_x \) the total amount of material, i.e., ice plus water, and \( k \) the rate constant per mass unit.

We will ignore in this paper that ice is also formed on the existing interface. This gives a term proportional to \( n^\alpha \) where \( \alpha = 2/3 \) if the surface is smooth, and larger if we consider a surface characteristic for dendrite growth. Such surfaces are of dimension between 2 and 3 as illustrated in the book of Mandelbrot [5]. However, the experiments of Clausse and Broto were done on very small droplets, and for values of \( \alpha \) near one, the extra term will not modify the features of the equation very much.

The solution of eq. (1) is easily obtained. As can be seen already from the differential equation: the initial rate of growth is unequal to zero. This contradicts the experiments. Fig. 1 shows that the slope is increasing from almost zero, rather than decreasing from a given initial value as follows from (1). Fig. 1b is introduced to show that the phenomenon is not restricted to water.

In order to describe this acceleration, the equation

\[ \frac{dn}{dt} = kn(n_x - n) \]  

(2)

was proposed in ref. [2]. This equation expresses the fact that the effective rate “constant” \( kn \) is itself proportional to the amount of ice already present. The solution is

\[ n(t) = n_x - \frac{n_0}{n_x - n_0} \exp(-n_xkt). \]  

(3)

where \( n_0 \) is the value of \( n \) at \( t = 0 \). Although the general form of \( n(t) \) follows the experimental points far better than (1) the solution shows that no ice is formed at all if \( n_0 = 0 \), as can be seen immediately from the differential equation. Since there is no indication that \( n_0 = 0 \) when the system has reached the supercooled state this rules out eq. (2).

A more flexible assumption is to take the rate constant to be an arbitrary function of \( n \), and hence of \( t \):

\[ \frac{dn}{dt} = k(t)(n_x - n) \]  

(4)

the solution is

\[ n(t) = n_x - (n_x - n_0) \exp\left(- \int_0^t k(t') \, dt'\right). \]  

(5)

Assuming that \( k(\infty) \) is constant, let us introduce a variable rate constant that is low initially and increases when time goes on:

\[ k(t) = a \exp(-t/\tau_2) + k_x, \]  

(6)

where \( a \) is an arbitrary constant and where \( \tau_2 > 0 \) is the “build up” time to reach the asymptotic value. If \( a \approx k_x \) the initial rate is very slow, as observed in the experiment.

Eqs. (4) and (6) can be cast in a different
picture: Suppose we introduce a hypothetical substance \( m \) that is spontaneously formed in the supercooled liquid and suppose that this substance governs that rate at which ice is formed. In mathematical form:

\[
\frac{dn}{dt} = \tau_1^{-1} m (n_0 - n), \tag{7a}
\]

\[
\frac{dm}{dt} = \tau_2^{-1} (m_0 - m). \tag{7b}
\]

The solution of the second equation leads to an effective rate constant, given by

\[
k(t) = \frac{m(t)}{\tau_1} = \tau_1^{-1} (m_n - (m_n - m_0) e^{-t/\tau_2}) \tag{8}
\]

in the first equation. If \( m_0 = 0 \) we observe that during the time period \( t < \tau_2 \) the rate is small, and for \( t > \tau_2 \) the rate is \( k \approx k_\infty \). Hence the time \( \tau_2 \) could be called the incubation time of the system. The general shape of the curve obtained for \( n(t) \) is in accordance with the experiment (see fig. 1) and there is no need to assume that \( n_0 \neq 0 \).

The possible interpretation of the substance \( m \) depends on whether the observed curve is a special property of water or whether the curve is a general property of all supercooled liquids. We assume it is a general property and suggest that \( m \) represents an intermediate phase: a “sloppy crystal”, out of which the ultimate crystal is formed. In the case of water it could be that the intermediate phase is associated with a strongly correlated H-bond orientation, a phenomenon suggested by Angell [7] to explain the Kauzman paradox, a model later taken up by Stanley and Teixeira [8]. The experiments on benzene [3] seem to indicate that the behavior is not particular to water, since the curves have the same general shape.

Four, entirely different observations seem to justify the hypothesis for the intermediate substance. First is the Ostwald [9] step rule. Ostwald argued that the undercooled liquid is a metastable system and that such a system will not undergo a direct transition to the stable ground state, but that it will be much more likely to undergo a transition to states that can be easily reached in phase space. Experimental indication for the existence of several intermediate phases can be found in the work of Bizid et al. [10] and Defrain [11].

Secondly, evidence for an intermediate state may be found in the experiments of Bilgram [12]. In this work, ice is formed at a constant rate in a flat front. The layer above the front is observed by means of light scattering, the layer has properties distinctly different from water. A third piece of information is of a similar nature, but comes from computer experiments of Landman et al. [13]. They use a cold substrate of solid with a liquid above it. Instead of the traditional periodic boundary conditions in all three directions, the system is periodic in only two directions. This also indicates a set of surface layers with properties different from both the solid and the liquid.

The last item of evidence is more speculative. Speedy [14] has argued in a recent paper that the curve of the upper stability limit of the superheated liquid and the curve of the lower stability limit of the supercooled liquid meet at low pressures, i.e. they form one continuous curve. Since it is impossible that the gas state can go over in a continuous way into the solid state, this seems also to indicate that there must exist at least one intermediate state.

Eqs. (7) lack a feedback term, that is eq. (7b) should contain a term \(-pn\), where \( p \) is the rate at which \( n \) is produced, to express the fact that \( m \) is consumed to make ice. The resulting equation cannot be solved explicitly. It is clear that the effect will be a diminishing amount of \( m \), when more and more \( n \) is produced, i.e. the effective rate in (7a) will slow down again and may become even zero. Also, there is a second process by which ice is formed namely through surface growth as mentioned above.

It was pointed out to us that the idea that one system triggers another, can also be found in axonal membranes [15]. The rate constants of the Hodgkin and Huxley model for potassium ion conductance in squid axons have been found to depend on time due to an “after effect” of the jump voltage. The resulting curves show a similar onset-time in the current density.
3. The precooling experiment

A modification of the constant temperature process was introduced by Clausse and Broto [4]. In this experiment the sample was held at T₁ for a certain length of time, then the temperature was raised to T₂; see fig. 2. Both T₁ and T₂ are below the fusion temperature Tₘ. We will refer to this as the precooling experiment. It was found that the incubation time in this experiment is shorter than the time needed to observe ice formation in an experiment where the sample was kept at T₂ all the time, i.e., an experiment without precooling. This seems to suggest that τ₂ is temperature dependent in the following manner: The incubation time τ₂ is very large at the melting temperature and diminishes rapidly at lower temperatures. The issue of whether this behaviour is reproduced in Molecular Dynamics experiments is discussed in ref. [16].

Consequently during the time that the sample is kept at the lower temperature T₁, more m is created than if it were held at T₂ during the same time interval. Since a certain amount of m has been created at time t₀, the result is that the process at temperature T₂ starts off with m₀ ≠ 0. The ice formation is given by

\[ n(t) = n₀ + (n₀ - nₙ) \exp[-mₗt/τ₁] + (τ₂/τ₁)(m₀ - nₙ)(e^{-κτ₂} - 1), \]  

where n₀ = 0, since we assume that the ice formation during t ≤ t₀ at T₁ is negligible.

A sequence of precooling experiments should be done to establish m(T₁, t₀) = m₀ for various durations of the precooling t₀ at different temperatures T₁.

What is known at present is the result for one given temperature T₁ and for two time constants t₀. One experiment [4] was done with a t₀ of 5 min. This experiment seems to indicate that m₀ depends very little on t₀ for the value of T₁ chosen, i.e., increase from the value used in the first run, does not influence the behavior at T₂ noticeably. This means that m seems to be "saturated" in the experiment that used the short t₀ and leads to an upper limit of τ₂ at the temperature used in the experiment. Note that although m has reached its maximum at T₁, it may not be at its maximum at T₂. The important thing is that m₀ ≠ 0 at t₀. This means that the solidification curve for times beyond t₀ should start with a small but finite slope. The scatter of the experimental data does not allow us to see whether this prediction is confirmed.

The other experiment [17] used a t₀ of 1 min. In this case no shortening of the onset time was observed. Hence for given T₁ we find that 1 min < τ₂ < 5 min.

4. Constant cooling experiment

Suppose we perform an experiment in which the sample has a temperature Tₘ at t = 0 and is subsequently cooled at a constant rate R. At t' the temperature is kept constant, i.e.,

\[ T(t) = T_M - Rt, \]
\[ T₁ = T_M - Rt' \]

and we compare this experiment with an experiment wherein the temperature was kept at T₁ at all times. The question is which of these two leads to a shorter incubation time before ice is formed.

In order to estimate this time, we assume a
functional dependence of the relaxation time on the temperature as given by

$$\tau_2 = A(T_M - T)^{-\alpha},$$

(11)

where $A$ is the undetermined amplitude and $\alpha > 0$ is a constant. This formula serves no other purpose than to describe the observation that $\tau$ is infinite at $T = T_M$ and rapidly decreasing for lower temperatures. Although this expression is at variance with expressions found in the literature, the exact form is not very relevant for the argument that follows:

Inserting (10) into (11), gives for (7b)

$$\int dm/(m_s - m) = A^{-1} \int_0^t (T_M - T(t))^\alpha dt$$

$$= \frac{A^{-1}}{\alpha + 1} (Rt')^{\alpha t'};$$

(12)

substituting (10) and (11) leads to

$$m = m_s + (m_0 - m_s) \exp\left[-(t'/(\alpha + 1))\tau_2\right].$$

(13)

Let us compare this result with the result we obtain if the sample is instantaneously cooled to $T_f$. At time $t'$ the constant-cooling-experiment result (12) has a value of $m(t')$ as if the effective incubation time were $(\alpha + 1)\tau_2$, which is smaller. Consequently less $m$ is present and the formation of ice, as governed by eq. (7a), is also lagging behind.

If one compares a slow cooling experiment with a fast cooling experiment, then the slow cooling leads to a longer $t'$ and consequently a larger value of $m$. This is in accordance with the experimental observation, that at least for $T > -40^\circ C$, the general trend seems to indicate that the probability of crystallisation is enhanced in a slow cooling experiment.

Note added in proof

It was brought to our attention, by Dr. David Turnbull, that we overlooked an important effect which may prove to give an alternate explanation of the observations made in the precooling experiment. If one has ice crystals (or water droplets) suspended in the oil of the emulsion it has been observed that the bigger droplets grow bigger at the cost of the smaller droplets. This process is called Ostwald ripening. Despite the fact that water seems not to dissolve in the surrounding oil, the solubility is never completely zero, consequently water molecules can transfer from one droplet to another. The chemical potential of the big droplets is smaller than the chemical potential of the small droplets and this acts as a thermodynamic driving force which transfers water from the first to the second. The result is that, when time goes on, the bigger droplets grow at the expense of the small ones. Since solubilities, diffusivities and chemical potentials are all dependent on the temperature, this effect cannot be easily separated from the mechanism we propose until more data are available.

Also we would like to point out that the simple rate equation (1) corresponds to eq. (7.17) in Hobbs [18]. In this reference there is a complete description as to how the rate constant depends on the temperature. Since the rate of nucleation depends on the sizes of the droplets and this acts as a thermodynamic driving force which transfers water from the first to the second. The result is that, when time goes on, the bigger droplets grow at the expense of the small ones. Since solubilities, diffusivities and chemical potentials are all dependent on the temperature, this effect cannot be easily separated from the mechanism we propose until more data are available.

Also we would like to point out that the simple rate equation (1) corresponds to eq. (7.17) in Hobbs [18]. In this reference there is a complete description as to how the rate constant depends on the temperature. Since the rate of nucleation depends on the sizes of the droplets, the behaviour will depend on the distribution of sizes. It was demonstrated by Clausse that the rather narrow distribution of radii cannot explain the growth curves displayed. Consequently we believe that eq. (1) cannot be used to explain the data.

References

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