

The freezing of water

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The structure of the water molecule and the ways in which water molecules combine to form ice and water are discussed and it is concluded that water is best pictured as consisting of a mixture of molecules bonded into 'flickering clusters' together with a proportion of non-bonded molecules. The structure changes which must occur on freezing are examined and the theories of homogeneous and heterogeneous nucleation are outlined. It is concluded that, though a detailed understanding of the freezing process has not yet been achieved, a reasonably effective phenomenological description can be put forward.

1. Introduction

Water is, from many points of view, one of the most interesting and important substances on this planet and it occurs in huge quantities, often with a purity rarely found in other substances outside the laboratory. This unique importance is due in part to the chemical properties of water but also in large measure to the fact that its freezing point and vapour pressure are such that solid, liquid and vapour phases all exist in substantial quantities. The transitions between these phases are responsible for many processes occurring near the Earth's surface and may have played a vital part in the long chain of events leading to the phenomenon of life.

I shall not be concerned here with any of these broader issues but concentrate on one small facet of the behaviour of water—the way in which it freezes to form ice. It might seem that this is almost a trivial problem but we will see that not only is there a great deal of physics involved but we are still a long way from really understanding many of the processes on a molecular scale.

The experimental facts can be briefly summarized. Water in large quantities freezes to ice at 0°C at ordinary atmospheric pressure. The ice which forms has a hexagonal crystal structure and is slightly less dense (0.917 g cm⁻³) than liquid water. This represents only one point on the phase diagram, of course, and experiments at high pressures by Tammann¹ and by Bridgman² have revealed a total of six other forms of increasingly compact crystal structure together with a cubic modification of the ordinary ice structure which is stable at low temperatures.^{3,4} For the most part we shall be concerned only with ordinary hexagonal ice which is designated Ice I_h.

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When we come to look at the freezing transition more carefully, however, we find that it is often possible to supercool small volumes of clean water to well below 0°C before they suddenly freeze. This phenomenon of supercooling is found to occur in most pure liquids and the amount of supercooling possible increases as the volume of liquid is decreased and as its purity is improved. Experiments to measure the maximum amount of supercooling possible have been particularly extensive in the case of water and Fig. 1 gives a picture of the

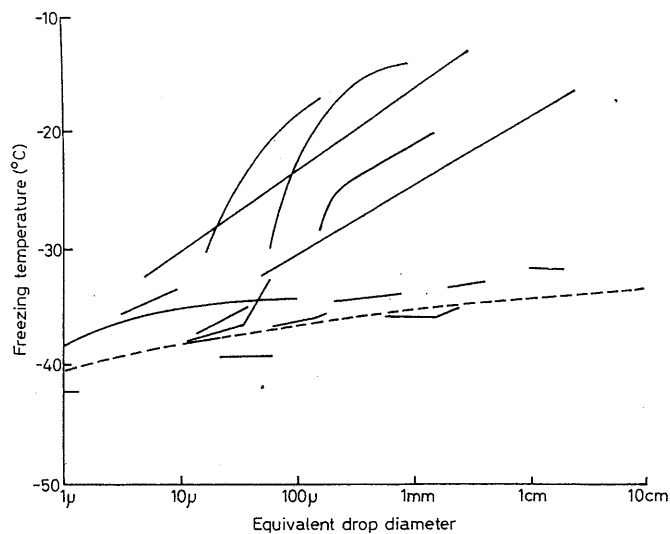


Fig. 1. Greatest supercooling obtainable for pure water droplets of given size, as found by various workers (full lines). The broken line is the homogeneous nucleation threshold calculated from equation (6).

results obtained by different workers using widely different methods of supporting the water droplets and protecting them from outside contamination. It can be seen that there is a reasonably consistent lower limit to the temperature which can be reached and it seems reasonable to explain the results of those experiments which gave higher freezing temperatures as due to some form of contamination of the sample.

A theory of freezing must therefore explain not only the equilibrium freezing point of 0°C but also the fact that small droplets of clean water can be supercooled to about -40°C before they freeze, while larger drops and drops containing suspended impurity particles begin to freeze at some intermediate temperature. In the following sections we shall outline this theory in its present state.

2. Structure of ice and water

Whilst it is possible to treat the freezing of water using a generalized theory in which the properties specific to water are introduced as parameters which can be chosen to give the best agreement with experiment, this is not a very satisfactory way to proceed. We shall, indeed, be forced back to this sort of theory for some of our discussion but we shall first go as far as possible while still taking into account the peculiar structure and properties of the material with which we are dealing.

The water molecule-hydrogen bonding

A simple treatment of the electronic structure of the water molecule is given in standard texts on molecular physics.⁵ The electronic configuration of an oxygen atom can be written $O : (1s)^2 (2s)^2 (2p_z)^2 (2p_x) (2p_y)$ and that of hydrogen is simply $H : (1s)$. If two hydrogen atoms H_I and H_{II} are placed on the x and y axes, then their electrons interact with the p_x and p_y electrons of the oxygen atom to give combined orbitals of the form

$$\begin{aligned}\psi_I &= \psi(H_I:1s) + \lambda\psi(O:2p_x) \\ \psi_{II} &= \psi(H_{II}:1s) + \lambda\psi(O:2p_y)\end{aligned}\tag{1}$$

where λ is a parameter reflecting the degree of polarity of the bonds. These orbitals are directed along the x and y axes and, to a first approximation, bind the molecule as shown in Fig. 2(a), with an H—O—H bond angle of 90° . The 'lone-pair' electrons on the oxygen atom extend along the $\pm z$ directions in $2p_z$ orbitals.

This is, however, only a first approximation. The electron distribution in the bonds does not exactly balance the charge of the protons, so the bonds repel each other to give an H—O—H angle which is observed to be $104^\circ 31'$. This has its effect on the electron wave functions and a certain amount of ($O:2s$) becomes mixed in with them as an additional term in equation (1). When the constants involved, such as λ , have been adjusted to give minimum energy, the bonding angle has its observed value and the shape of the molecule is as shown in Fig. 2(b). The lone-pair electrons are effectively hybridized as well and give electron density maxima in directions approximately tetrahedral with the O—H bonds. This effect has been worked out in detail by Pople.⁶

The result of this discussion is to see that the water molecule is approximately tetrahedral in shape with two positive vertices where the protons are located and two negative vertices caused by the lone-pair electrons. This tetrahedral shape is fundamental to the binding together of water molecules. In the configuration of lowest energy they will be arranged with oppositely charged vertices adjacent and the coordination number will be four.

The bonding together of water molecules is not, however, entirely due to

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electrostatic attraction. Rather it seems that the bonding of another molecule causes a further re-arrangement of the molecular wave functions so that they become further hybridized and their orientations approach more nearly the ideal tetrahedral angle of $109^{\circ}28'$. In ice, when each molecule is bonded to its four nearest neighbours, this ideal angle is reached within experimental error—a change of nearly 5° from the configuration of an isolated molecule. Thus, as pointed out by Frank,⁷ the bonding between water molecules appears to be

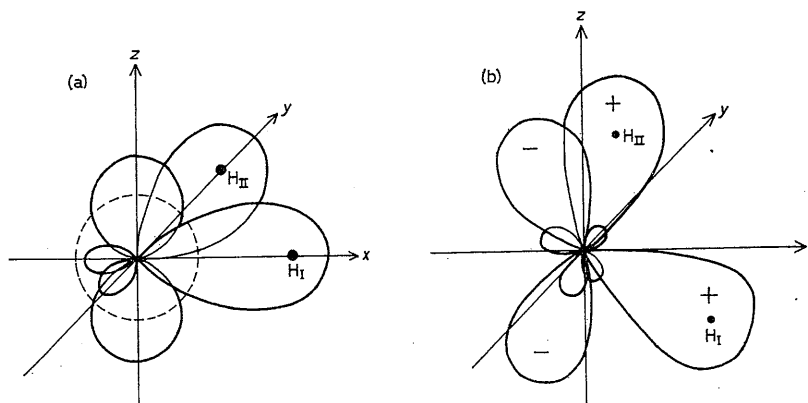


Fig. 2. (a) Orbital configuration of outer electrons in water molecule to a first approximation, neglecting interaction with $O:(2s)^2$ electrons which are shown in broken lines. (b) Approximately tetrahedral orbitals in water molecule resulting from hybridization. In both cases the orbital shapes are roughly schematic only.

partly covalent rather than simply electrostatic. The bonding is, in addition, a cooperative phenomenon, in that the forming of one bond tends to stabilize other bonds formed by the molecule. This has important consequences in the theory of the structure of liquid water.

Structure of ice

The structure of Ice I_h was investigated by Barnes⁸ in 1929 but, because of the small X-ray scattering power of hydrogen, he was only able to locate the positions of the oxygen atoms. These lie in a complex hexagonal array, as shown in Fig. 3(a). Each water molecule has four nearest neighbours, as we would expect, and the whole structure is thus very open when compared with the twelve-fold coordination of close-packed spheres.

Determination of the proton positions had to await the development of electron- and neutron-diffraction techniques, though various possible models were put forward on indirect evidence. The model finally confirmed by experiment was that of Pauling,⁹ who proposed that the structure was a random or statistical one, limited only by the following rules which had been used in an

earlier model due to Bernal and Fowler¹⁰: (i) There is one proton on each O—H— — —O bond and it is nearer to one end of the bond than to the other, and (ii) each oxygen has two 'near' protons and two 'far' protons on its four bonds.

Using these rules it is simple to make an approximate evaluation of the number of possible proton arrangements associated with a large number N of molecules. The total number of bonds is $2N$ and there are two possible proton positions on each bond giving 2^{2N} arrangements. However, of the sixteen possible proton configurations round a particular oxygen atom, all but six violate rule (ii). The total number of acceptable arrangements is thus $(6/16)^N \times 2^{2N}$

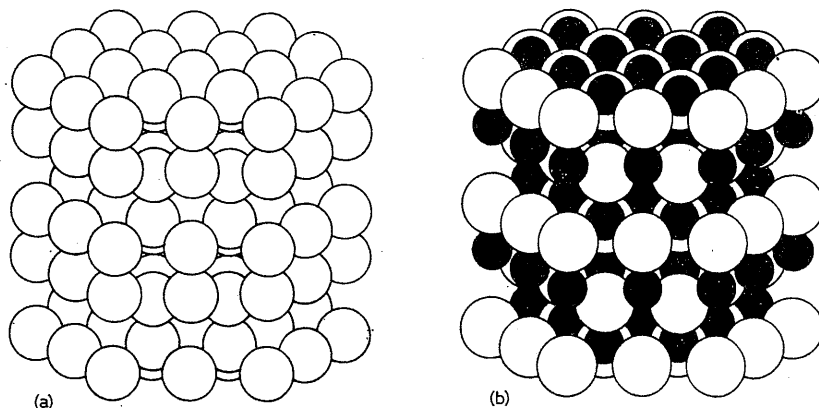


Fig. 3. Atomic models, to the same scale, of: (a) Ice I_h and (b) Silver iodide. In the latter case the black spheres represent silver atoms.

or $(3/2)^N$. Recently more sophisticated combinatorial methods have shown this result of Pauling to be in error by about 2 per cent but this is not important. The significance of the result for our present purpose is that the large number of possible configurations makes a contribution to the entropy of $k \log(3/2)$ per molecule, which has a considerable stabilizing effect on the structure. Since it is possible for protons to move in the structure by quantum tunnelling along the bonds or from bond to bond, the whole proton configuration is constantly changing at ordinary temperatures, though it becomes 'frozen' as the temperature is reduced towards absolute zero. This anomalous residual entropy has been experimentally verified¹¹ and agrees well with Pauling's calculation.

The statistical model has been confirmed by electron and neutron diffraction experiments^{12,13} which show a 'half-hydrogen' at each of the possible positions on the bond. The proton is found to be about 1.0 \AA from one oxygen and 1.75 \AA from the other. The structure is shown in Fig. 4 on an expanded scale.

It might be of interest, in passing, to comment on the structures of some of

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the other forms of ice. The cubic modification stable at ordinary pressures and low temperatures, Ice I_c , differs from Ice I_h only in the packing of successive molecular layers, the oxygen atoms now occupying a diamond cubic structure. It too has a statistical distribution of protons on the bonds¹⁴ and the same configurational entropy as Ice I_h . The high pressure ices have atomic arrangements which tend to give a closer packing, the hydrogen bonds being necessarily distorted in the process. Not all of these show proton disorder.⁴⁰ The most

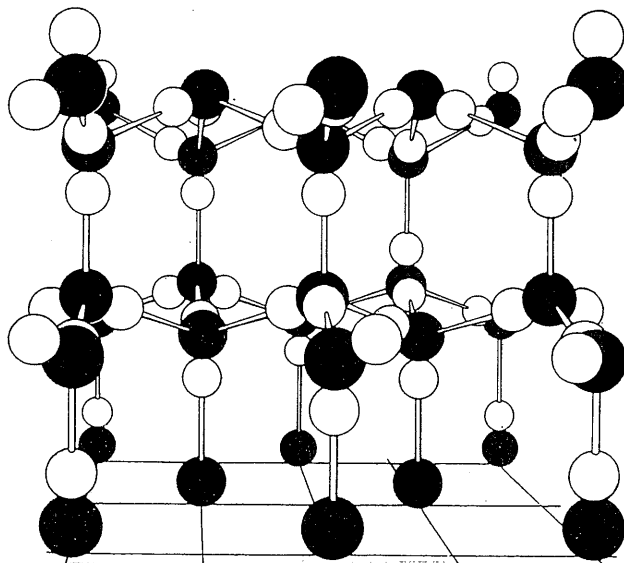


Fig. 4. An expanded view of the Ice I_h structure. White spheres represent protons in random positions. (After Buswell & Rodebush.⁴³)

dense form, Ice VII, consists essentially of two interpenetrating Ice I_c lattices and is thus able to maintain its tetrahedral bonding but to achieve a more nearly close-packed structure.⁴¹ A discussion of some of these ices and their interconversion has been given recently by Bertie, Calvert & Whalley.⁴

Structure of water

The theory of the structure of liquids is much less well developed than the analogous theory for solids and, among the liquids, those with complex molecules are usually more difficult to treat than atomic liquids like the liquid metals. Part of the difficulty lies with the lack of experimental information. Diffraction studies, instead of giving atomic positions, simply yield a distribution curve giving the probability of finding a molecule at a given distance from its

neighbours. The number of molecules with their centres at distances between r and $r + dr$ from a chosen molecule can be written:

$$n(r) = 4\pi r^2 g(r) n_0 dr \quad (2)$$

where n_0 is the average number density of molecules in the liquid and $g(r)$ is the distribution function. X-ray measurements by Morgan & Warren¹⁵ have determined the function $g(r)$ for water at various temperatures. Two such curves are shown in Fig. 5. The positions of the first few neighbours for ice are shown

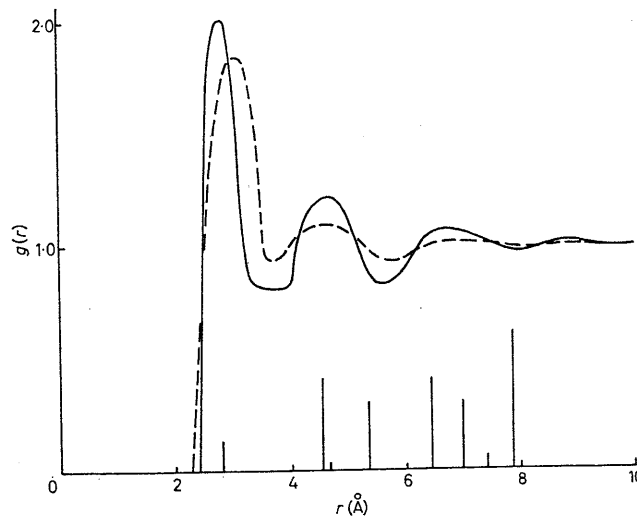


Fig. 5. The radial distribution function $g(r)$ for water at 1.5°C (full line) and 83°C (broken line).¹⁵ The radial distances for molecules in the Ice I_h structure are also shown, the line lengths being proportional to the number of molecules at that distance.

in the same diagram. It is clear that there is a certain correspondence between these positions and the locations of humps in the curve for $g(r)$, particularly at low temperatures, and it is tempting to picture water as having a somewhat ice-like short range order which is progressively broken up as the temperature is raised.

Most models of liquid water are forced to begin from some pictorial idea such as this. An explicit model is then formulated and its distribution function compared with the experimental $g(r)$. If this is satisfactory, further predictions of thermodynamic and other quantities can be made and compared with experiment. A great variety of starting points for such models have been used in this way, all assuming that there is considerable hydrogen bonding in water at low temperatures and that at higher temperatures the liquid becomes more close

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packed. The models differ in the way they picture this process. A recent review has been given by Kavanau.¹⁶

The most generally satisfying picture of liquid water structure seems to be some modification of the 'flickering cluster' model proposed by Frank & Wen^{7,17} and since developed in some detail by Némethy & Scheraga¹⁸ and, from a somewhat different viewpoint, by Marchi & Eyring.¹⁹ The basis of this picture is that, because of the cooperative nature of hydrogen bond formation, the molecules in liquid water can be divided into two species—those which belong to hydrogen bonded clusters and those which are unbonded. The membership of each class is, of course, constantly changing and an individual cluster may have a lifetime only of order 10^{-11} sec, a time which is, however, long compared with the scale of molecular motions. The calculations of Némethy & Scheraga suggest a mean cluster size of about ninety molecules at 0°C. About 30 per cent of the total number of molecules have full tetrahedral bonding and 24 per cent are unbonded at this temperature, the remainder having mostly either one or three bonds. The cluster size decreases at higher temperatures, as is expected, and is estimated to be about twenty molecules at 100°C with 44 per cent of all molecules being unbonded. The clusters, while having largely tetrahedral bonding, are, of course, not necessarily ice-like in structure.

Other models of water structure have been proposed, including forms involving bent hydrogen bonds^{10,20} or with rather highly organized sub-structures such as the pentagonal dodecahedra proposed by Pauling²¹ by analogy with the structure of methane hydrate or sheets of puckered ice-like hexagonal rings.^{22,42} These models, though possessing some virtues and undoubtedly representing possible instantaneous structures over small volumes, seem rather less attractive than the more random flickering cluster model.

In our subsequent discussion we shall be concerned with the properties of water in the supercooled state. All the experimental evidence indicates that the properties of supercooled water are simply those of normal water extrapolated to lower temperatures and indeed, except for the possibility of freezing, there is no reason to expect any sort of discontinuity in properties at the freezing temperature.

3. Homogeneous nucleation of ice crystals

Liquid water contains, as we have seen, a large variety of hydrogen bonded clusters. These will differ not only in size but also in molecular arrangement and, among them, those clusters which have an ice-like arrangement of molecules are of particular importance. Such clusters may be in a very small minority since, as Pauling has shown,²¹ other arrangements of small numbers of water molecules can form much more favourable bonding patterns. They are important, however, because at temperatures below the equilibrium freezing point they

may occasionally grow by statistical fluctuations to a size at which they are stable relative to liquid water. They can then develop into macroscopic ice crystals.

Consider, in a supercooled liquid, such an ice-like cluster containing i molecules. These, because of the thermodynamic stability of ice relative to water at this temperature, have a lower free energy than an average molecule in the liquid, except for those at the surface of the cluster which make a positive contribution which is proportional to $i^{2/3}$. The total free energy of the cluster relative to the same i molecules in the average liquid state is thus:

$$\Delta G_0 = Ai^{2/3} - Bi \quad (3)$$

A and B depend on temperature and on the shape of the cluster. Because the ice structure can be added to without internal bond rearrangement we can use

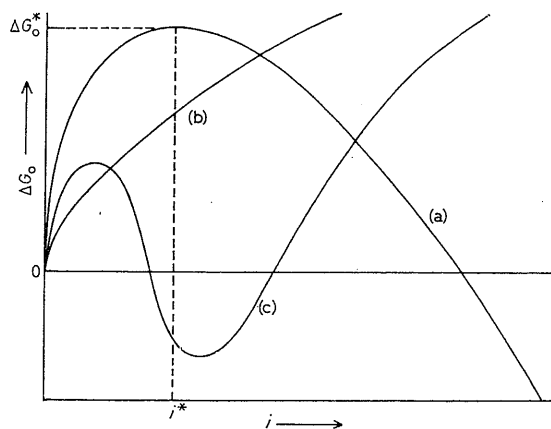


Fig. 6. Free energy ΔG_0 of a cluster containing i molecules: (a) in an ice-like structure, (b) in a non ice-like structure, and (c) in a structure giving optimum bonding when small in size. In all cases the temperature is assumed to be below 0°C and the curves only have meaning for integral i .

this equation for ice-like clusters of all sizes and the variation of ΔG_0 with i is as shown in curve (a) of Fig. 6. Small clusters are unstable and tend to disappear rather than grow. Once a critical size i^* is reached, however, the addition of further molecules lowers the total free energy of the system and the cluster can develop quickly into a macroscopic crystal. The maximum in the value of ΔG_0 , which we call ΔG_0^* , gives the height of the thermodynamic barrier to nucleation.

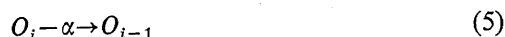
Other types of cluster with different structure can be treated in the same way but either the basic structure has high energy which changes the sign of B , as in curve (b), or, because the bonding must change if the cluster is to grow, B is not constant and we may have a situation such as in curve (c) where small clusters are stable but large ones are unstable.

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The development of ice-like clusters into stable nuclei cannot be treated as an equilibrium problem but is rather one in which a whole set of growth and melting equations must be solved. Thus a cluster O_i of i molecules may gain a molecule according to an equation of the form



where α is an unbonded molecule, or it may decrease in size as



For either of these reactions to take place the molecule α must move from a non-bonded to a bonded state, or vice versa, and in the process it will always have to pass through an energetically unfavourable configuration of excess free energy Δg , say. This quantity is related to, and in simple cases is identical with, the free energy barrier to diffusion processes in the liquid. In water it is roughly equal to the energy associated with a hydrogen bond.

The solution of equations of this type was originally carried out by Becker & Döring^{23,24} as an improvement to an earlier theory by Volmer.²⁴ Since then the matter has been taken up by Frenkel and others,²⁵ and a solution specially applicable to liquid/solid transitions has been given by Turnbull & Fisher.²⁶ Their result is, for a simple liquid,

$$J = n^*(A/9\pi)^{\frac{1}{2}} (NkT/h) \exp [-(\Delta G_0^* + \Delta g)/kT] \quad (6)$$

where J is the rate of formation, per second, of freely growing nuclei in a volume containing N liquid molecules, n^* is the number of surface molecules in a cluster of critical size and h is Planck's constant.

This formula also admits of a simple pictorial interpretation. $(\Delta G_0^* + \Delta g)$ is the free energy excess of a cluster of critical size which is about to gain a further molecule. $Nn^* \exp [-(\Delta G_0^* + \Delta g)/kT]$ is then roughly the number of clusters we would expect to find in this condition in the volume considered and (kT/h) , which has the dimensions of a frequency, gives the rate at which the activated molecule can move to join the cluster. The quantity $n^*(A/9\pi)^{\frac{1}{2}}$ is usually within a factor 10 of unity.

For 1 cm³ of water $(nkT/h) \sim 10^{35} \text{ sec}^{-1}$ so that if this volume of water is to remain unfrozen for as long as one second we must have $(\Delta G_0^* + \Delta g) \approx 76kT$. If we can work back to evaluate ΔG^* in terms of supercooling, using a specific model for the cluster and equation (3), then we can determine the lowest temperature to which this volume of water can be supercooled before its probability of freezing in a few seconds becomes very high. Because of the very large magnitude of the pre-exponential factor in equation (6), J varies very rapidly with temperature and this nucleation threshold is very sharply determined.

The difficulty now is to evaluate the quantities A and B in equation (3). The cluster for which this is necessary contains a few tens of molecules and is

thus rather difficult to treat. It is not large enough for it to be valid to apply macroscopic concepts like surface or volume free energy except in very rough approximations and, at the same time, lack of detailed knowledge of water structure makes any calculations at molecular level very uncertain.

For want of a better method many authors^{24,27} simply ignore molecular considerations and use a continuum approach. If we suppose the cluster to be spherical, which is almost certainly a good approximation in this size range, then equation (3) is replaced by

$$\Delta G_0 = 4\pi r^2 \sigma - \frac{4}{3}\pi r^3 \Delta G_v \quad (7)$$

where σ is the free energy per unit area of ice-water interface and ΔG_v is the difference in free energy per unit volume between ice and water at supercooling ΔT . The thermodynamic relation $S = -(\partial G/\partial T)_p$ allows us to write

$$\Delta G_v = \int_0^{\Delta T} \Delta S_v d\Delta T = \overline{\Delta S}_v \Delta T \quad (8)$$

where $\overline{\Delta S}_v$ is an average of the entropy of fusion over the supercooling range ΔT . This can be approximated by

$$\overline{\Delta S}_v \approx (1.13 - 0.004\Delta T) \times 10^7 \text{ erg cm}^{-3} \text{ deg}^{-1} \quad (9)$$

Maximization of ΔG_0 from equation (7) then gives:

$$\Delta G_0^* = \frac{16\pi\sigma^3}{3(\overline{\Delta S}_v \Delta T)^2}$$

and, when substituted back in equation (6) with $J \approx 1 \text{ sec}^{-1}$, this allows the nucleation threshold to be found. The broken curve in Fig. 1, which is drawn for $\sigma = 22 \text{ erg cm}^{-2}$ to give best fit, shows that the experimental results can be fitted very well by this simple theory. The parameter σ has a physically reasonable value but cannot be taken too seriously in view of the approximations involved.

4. Heterogeneous nucleation of ice crystals

The theory outlined above explains in reasonable fashion the nucleation behaviour of extremely pure water. Most freezing however takes place with much less supercooling than this and it can only be concluded that some foreign influence aids the formation of ice-like clusters of more than critical size. Whilst it is known that strong electric fields or high-pressure sound waves have some effect on freezing, the mechanism is uncertain and we shall limit our discussion to the case of foreign materials, which may be present in two forms—as suspended particles and foreign surfaces or as dissolved molecules.

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There is some evidence that dissolved molecules have some effect upon the cluster structure of liquid water and it is reasonable to expect this to have some influence on freezing behaviour. In particular, if some solute ion or molecule acts to stabilize a small ice-like cluster, this should aid nucleation, in competition with the general lowering of the equilibrium freezing point produced by the solute concentration. Alternatively, if the solute material tends to disrupt the clusters or to form clusters of another kind, then the probability of ice formation should be further depressed. Experimental results in this field have varied, largely due to the possibility of contamination by small solid particles. Some of the most careful recent results are those of Pruppacher & Neiburger²⁸ who conclude that, for all the materials tested, the effect is to decrease the probability of ice-cluster formation and to decrease the nucleation temperature to slightly below the value expected from simple thermodynamic reasoning.

The most important nucleating agents thus appear to be foreign surfaces and suspended particles of insoluble material. The way in which they act is fairly clear. If the molecular geometry and chemistry of an insoluble surface is suitable, then an ice-like cluster bounded on one side by this surface and on the others by liquid will have a lower free energy than an independent cluster and its growth will be facilitated. The general requirement for an efficient nucleating surface would seem to be that the free energy of the interface which it forms with ice should be as low as possible. The statement of this condition in terms of macroscopic quantities is much more reasonable here since it turns out that, for nucleation at temperatures of -10°C or so, clusters containing thousands of molecules are required.

A simplified formal theory is now easily worked out in terms of the size and shape of the foreign particle and a parameter m , defined by

$$m = (\sigma_{\text{particle/water}} - \sigma_{\text{particle/ice}}) / \sigma_{\text{ice/water}} \quad (11)$$

The possible range of m is from -1 to $+1$. The free energy barrier to the growth of an ice cluster on the surface of a particle which has a characteristic dimension R can be shown to be

$$\Delta G^* = \Delta G_0^* f(m, R) \quad (12)$$

where ΔG_0^* is the free energy barrier to homogeneous nucleation given by equation (3) and the form of the function $f(m, R)$ depends in detail on the geometry of the particle and of the ice cluster.^{29,30} $f(m, R)$ is always less than unity and may approach zero, so that heterogeneous nucleation is always thermodynamically easier than homogeneous nucleation.

Fig. 7 shows the calculated nucleation behaviour of a spherical particle with an assumed homogeneous surface parameter m . The curves give the temperature below which such a particle will nucleate an ice crystal from supercooled water in less than 1 sec. This represents, of course, a very simplified

picture in which an energy of 22 erg cm^{-2} has been assumed for the ice-water interface in accord with the conclusions from homogeneous nucleation experiments. It can be seen that, to be an efficient ice nucleus, a particle must have a size greater than about 100 \AA and a surface parameter, m , greater than zero. These predictions have been generally verified experimentally.

Because of interest in ice nucleation for cloud seeding experiments a great deal of work has been done to understand the mechanisms controlling the

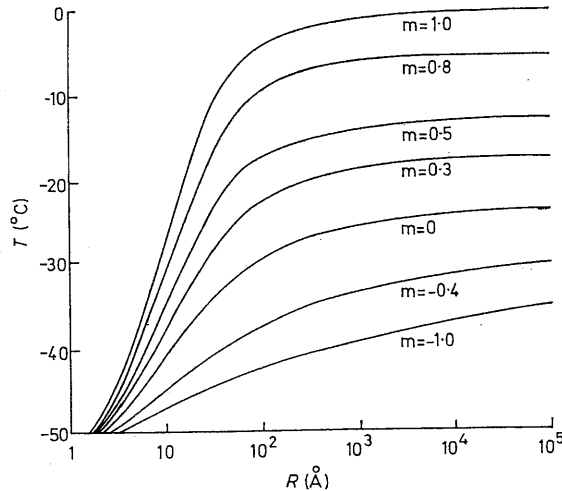


Fig. 7. Temperature below which a spherical particle of radius R and surface parameter m should nucleate an ice crystal from supercooled water in less than 1 sec. (Fletcher ²⁹.)

nucleation efficiency of various materials and to produce nuclei which will be active at minimum supercooling. A detailed discussion of these applications can be found elsewhere.³¹

There is general, though not universal,³² agreement that it is the parameter m and the shape and size of a particle which determine its nucleation efficiency, as outlined above. If m is to be as large as possible then, from equation (11), we require $\sigma_{\text{particle/water}}$ to be large and $\sigma_{\text{particle/ice}}$ to be small.

The first requirement suggests that the particle should tend to be hydrophobic or at least have a non-zero contact angle for liquid water. This indeed is found to be the case for most efficient nucleating materials such as silver iodide, which has a threshold at -4°C , and the newer organic nuclei³³ which may have even higher threshold temperatures. Theoretical treatment of this term is very difficult because of uncertainties in the water structure model.

The free energy $\sigma_{\text{particle/ice}}$ is more easily treated and indeed several general lines of attack have been used.³⁴⁻³⁶ The conclusion is that there is a

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deep minimum in the interface energy when the molecular geometry of the particle surface is in (1,1) correspondence with that of a low-index face of ice and less prominent minima near configurations of more complex fit.³⁶ As can be seen from Fig. 1, the symmetry of AgI is very similar to that of ice and the misfit is only about 1 per cent. The organic nuclei generally have more complex and poorer fit³³ but are so soft mechanically that the energy minima are very broad.³⁶ The importance of geometry rather than simply the chemical nature of the material involved has been strongly supported by the work of Evans,³⁷ though of course both affect the energy of the interface to some extent.

As well as the energy component of $\sigma_{\text{particle/ice}}$ we must consider any entropy contribution, and this may be of extreme importance because of the large configurational entropy of normal ice.³⁸ Any substrate which imposes orientational restrictions on its neighbouring ice cluster cannot be a good nucleus. This is abundantly supported by experiments with silver iodide which show that, if it is grown from solution with great excess of Ag^+ or I^- so that the surface charges are all of one sign, the nucleation efficiency is low, while, at the isoelectric point where equal numbers of ions of each sign are adsorbed, the efficiency is a maximum.³⁹ The OH bonding groups in the organic nuclei apparently do not cause any such entropy loss.

Conclusion

Our present understanding of the way in which water freezes is a rather incomplete one, largely because of difficulties in constructing a sufficiently detailed model of the structure of water and of the hydrogen-bonded clusters which form in it. It has proved possible to by-pass some of these difficulties by introducing suitable macroscopic parameters which then allows progress to be made in areas of practical interest. It seems certain, however, that better knowledge of this phase transition will come only when we have better knowledge of the structure of water and it is in this direction that much current research work is tending.

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