

HETEROGENEOUS NUCLEATION OF ICE CRYSTALS

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SYNOPSIS. A brief review is given of present understanding of the processes involved in the formation of ice crystals, concentrating on aspects likely to be of interest to metallurgists such as the nucleation behaviour of small particles, the effects of the surface topography of the nucleating substrate and the energetics of the interface between the substrate and the growing crystal.

1. INTRODUCTION

The presence of a paper on the physics of ice crystal formation in a symposium dealing mainly with the solidification of metals may seem rather strange. However, a great deal of work has been done in recent years on nucleation and growth of ice crystals and, from the nature of the problems involved, the approach has often been rather different from that common in the study of metals. It is the purpose of the present paper to summarize some recent work on formation of ice crystals, in the hope that some of the methods and conclusions, unfamiliar to metallurgists, may help to indicate some new ways of approaching familiar problems.

Experiments on the supercooling and freezing of water have been very carefully performed by many different workers, and it seems likely that we have a better quantitative knowledge of this process than for the freezing of any other liquid. The experiments consist of taking a small volume of water, protected from outside influences, and cooling it steadily until it freezes. By repeating the experiment a sufficient number of times a statistically reliable median freezing temperature or, in some cases, a supercooling limit can be found. The results depend very considerably on the purity of the water, the volume of the sample and, to a lesser extent, on the means by which it is contained. Liquid

volumes from 10^{-12} cm³ to 10 cm³ have been studied and the samples have been enclosed in glass tubes, supported on hydrophobic substrates or suspended at the interface between two immiscible liquids of suitable densities.

The results of some of these experiments are shown in Fig. 1. It can be seen that, although there is quite a wide spread of results, the maximum supercooling attainable for a particular sample volume has been determined quite consistently by a number of people and ranges from 41° for a droplet of 1 μm diameter to about 35° for a 2 cm drop. This behaviour can be interpreted very simply on the basis of classical nucleation theory. The maximum observed supercooling corresponds to the threshold of homogeneous nucleation, while freezing observed at the higher temperatures corresponds to heterogeneous nucleation on the supporting surfaces or on small particles of suspended material.

Most of the work which has been done recently on the freezing of water and the formation of ice crystals has concentrated on the behaviour of such heterogeneous nuclei, with the aims of understanding their action in detail and of producing ever more efficient "freezing nuclei". Most of the present paper will be concerned with this work.

2. MACROSCOPIC THEORY AND EXPERIMENT

The classical theory of nucleation behaviour was developed some thirty years ago by Volmer and Weber [2] and subsequently refined by Becker and Döring and by Zeldovich and Frenkel [3]. This theory, following the groundwork laid by Gibbs [4], assumes that macroscopic concepts such as surface free energy can be validly applied to small transient groupings of molecules. Once this is granted, then the free energy of formation of an embryo of the new phase having any arbitrary shape and size can be worked out and the distribution of such embryos determined by the methods of statistical thermodynamics. An examination of the kinetics of the molecules involved then gives the nucleation rate.

This procedure may be subject to a considerable amount of criticism in the case of homogeneous nucleation where the embryos are extremely small. In addition, it has re-

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cently been found necessary to apply certain rather large corrections [5] to the statistical treatment previously used. These problems are minimized in the discussion of heterogeneous nucleation where the embryos are normally much larger and the fixed number of foreign nuclei simplifies the statistics.

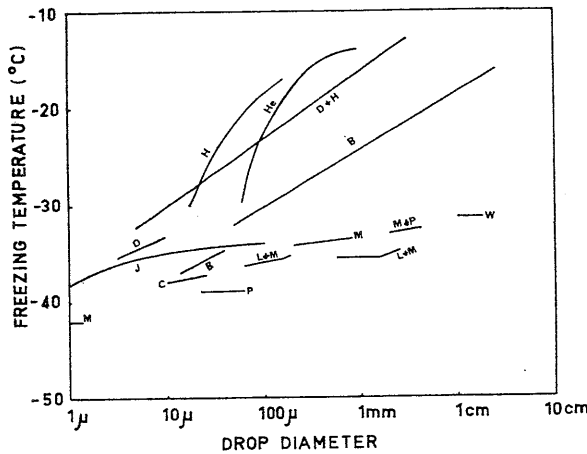


Fig. 1. Various experimental determinations of the freezing points of water droplets as a function of their size [1].

- B = Bigg
- C = Carte
- D = Day
- D & H = Dorsch & Hacker
- H = Hosler
- He = Heverley
- J = Jacobi
- L & M = Langham & Mason
- M = Mossop
- M & P = Meyer & Pfaff
- P = Pound
- W = Wylie

To illustrate the approach, consider a regular n -sided prism of the new phase 2 growing on a plane substrate 3 in an environment 1. The free energy of formation of this embryo, ΔG , depends on the interfacial free energies σ_{ij} and upon the free energy difference ΔG_v per unit volume between phases 2 and 1. An explicit expression can be written

$$\Delta G = \xi \pi r^2 h \Delta G_v + \xi \pi r^2 (\sigma_{12} - \sigma_{13} + \sigma_{23}) + 2\xi \pi r h \sigma_{12} \quad (1)$$

where

$$\xi = (n/\pi) \tan(\pi/n) \quad (2)$$

and the dimensions r and h are as shown in Fig. 2. The expression for ΔG is usually

simplified by introducing the quantity m , defined by

$$m = (\sigma_{13} - \sigma_{23})/\sigma_{12} \quad (3)$$

which specifies the degree of compatibility between the embryo and the substrate. m lies between -1 and $+1$ and approaches $+1$ for a completely compatible substrate.

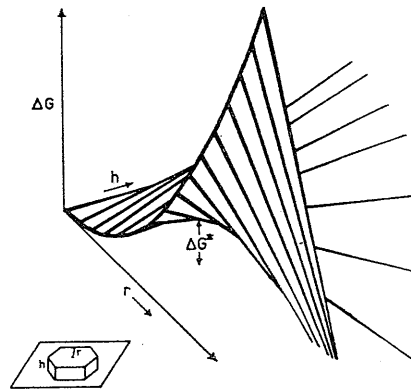


Fig. 2. The free energy of formation, ΔG , of a small prismatic embryo upon a nucleating substrate.

The form of the expression given for ΔG is clearly that of a ruled surface, as is shown in Fig. 2. In order that a free-growing crystal of the new phase may form, the embryo must grow from zero size, represented at the origin, through the saddle point where the energy is ΔG^* . It is this energy barrier that limits the nucleation process, and the nucleation rate can be written

$$J = K \exp(-\Delta G^*/kT) \quad (4)$$

where K is a kinetic constant which is determined in detail by the nature and concentration of the phases involved.

It is interesting to note that in this simple case, and also in cases where the substrate consists of two or three intersecting plane surfaces, the embryo maintains a constant habit during its growth and the path of minimum free energy through the saddle point is the intersection of the energy surface with a plane through the origin and perpendicular to the (r, h) plane.

The more general case, where nucleation occurs on a small foreign particle of arbitrary shape, can be treated similarly [6, 7]. In this

case the habit of the embryo does not remain constant, so that the analysis is more complicated. The final result, however, has the simple form for the nucleation rate of

$$J = K(R) \exp \left\{ -\Delta G_0^* f(m, R) / kT \right\} \quad (5)$$

where ΔG_0^* is the free energy barrier to homogeneous nucleation, R is a characteristic dimension of the particle involved and m is

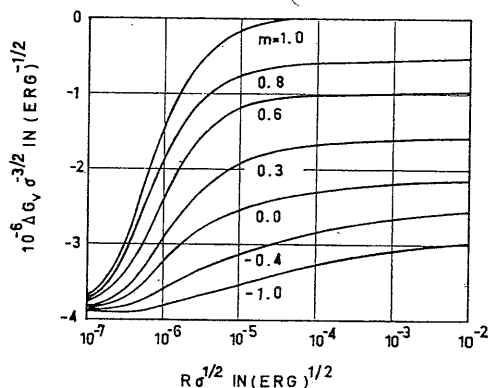


Fig. 3. Generalized nucleation curves for a spherical particle of radius R [7].

given by equation (3). The dependence of $K(R)$ on R is only weak. The form of the function $f(m, R)$ for several cases of interest is given in ref. 7.

For our present purposes it is more useful to consider, for a particle of given material (m) and size (R), the supercooling or supersaturation (ΔG_v) which is required in order that J become appreciable, say $J = 1 \text{ sec}^{-1}$ per particle. This has been plotted in Fig. 3 for the case of a spherical embryo growing on a spherical nucleating particle. Curves which are qualitatively similar can be derived for more complex geometries [7]. The curves in Fig. 3 are plotted in generalized form in terms of $\sigma \equiv \sigma_{12}$ and the free energy function ΔG_v .

To apply these curves to a specific situation requires simply a knowledge of the numerical values of the surface free energy σ and the compatibility parameter m and an explicit expression for ΔG_v in terms of supercooling or supersaturation [7]. When this is done for the case of the freezing of water ($\sigma \approx 20 \text{ erg cm}^{-2}$) then each unit on the ordinate scale corresponds to about 10°C while each unit on the abscissa scale is about 0.2 μm .

The efficiency of foreign particles as freezing nuclei thus drops sharply when their diameter is less than about 0.02 micron.

If, instead, we consider the formation of ice crystals by direct sublimation from water vapour which is in equilibrium with supercooled water — a situation of importance in cloud physics — then $\sigma \approx 100 \text{ erg cm}^{-2}$ and each unit of ordinate is about 100°C . Because

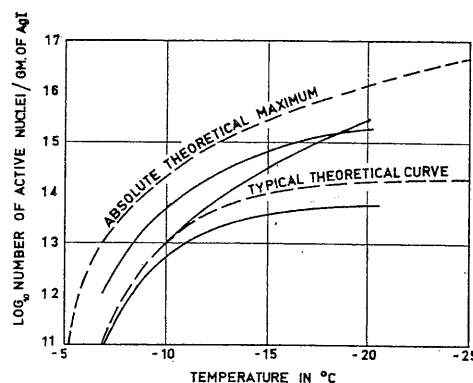


Fig. 4. Experimental (full lines) and theoretical curves for the nucleation activity of silver iodide smoke produced by several cloud-seeding generators.

of the great magnification of this scale only particles with m greater than about 0.8 are appreciably active as freezing nuclei and their efficiency is greatly depressed for particle diameters less than about 0.1 micron.

From curves of this kind it is relatively easy to calculate the nucleation behaviour of a population of particles of a single material distributed through a liquid or vapour. The threshold temperature at which large particles nucleate crystal formation gives a value for the parameter m and the size distribution can be observed directly, for example by electron microscopy. An analysis of this type has been carried out for aerosols of smoke particles consisting of silver iodide such as are used in cloud seeding experiments [8]. This smoke typically has a size range from less than 0.01 micron to perhaps a few microns diameter. The nucleation behaviour varies, of course, with the size distribution in the smoke but typical experimental results are as shown in Fig. 4. Also shown on the figure is a theoretical maximum curve below which all experimental results should lie, and a calculated curve for a typical smoke with a log-normal

particle size distribution with median radius 100Å and standard deviation $\times 2.5$. It can be seen that the general agreement is quite good.

3. MICROSCOPIC THEORY AND EXPERIMENT

The discussion in the last section might be described as macroscopic, in that the principal objective was to describe the nucleation behaviour of a population of particles in terms of their size and a simple parameter, m , characterizing their surface structure. To achieve a better understanding of the nucleation process attention should now be concentrated on phenomena of molecular scale. Again we shall base our discussion on progress which has been made in the study of nucleation of ice crystals. Experiments have been carried out by several groups on the nucleation behaviour of nominally plane substrates [9, 10]. These experiments are most conveniently made using growth from the vapour, though it cannot be immediately assumed that condensation does not occur as a precursor of ice crystal growth.

Several important results emerge from these experiments. First, as is to be expected, an appreciable supersaturation is required to nucleate crystal growth. Secondly, when crystals grow on a crystalline substrate they generally do so in one or more well-defined orientations. Thirdly, the crystals nucleate preferentially at steps or cracks in the surface of the substrate, showing preference for features 0.1 micron or more in height. The first result is inherent in the notion of a nucleation process. The second and third help to elucidate some of the molecular processes involved.

The free energy barrier to nucleation at a large step or re-entrant corner on an otherwise plane substrate of parameter m is easily worked out. For a hexagonal crystal the expression is complicated, but for a cubic crystal the result has a particularly simple form

$$\Delta G_n^* = \Delta G_0^* \left\{ \frac{1-m}{2} \right\}^n \quad (6)$$

where ΔG_n^* is the critical free energy for nucleation at a site where n substrate planes are mutually perpendicular. Thus, since $m > -1$, a plane substrate ($n = 1$) is favoured over homogeneous nucleation ($n = 0$), but a step ($n = 2$) or a re-entrant corner ($n = 3$) gives a still lower energy barrier. If

the surface features become smaller than the embryo itself, however, equation (6) no longer applies and the behaviour of the substrate approaches that of a plane surface.

It seems, both from experiment and from a simplified theoretical discussion, that the points of emergence of screw dislocations are unlikely to provide specially favoured nucleation sites. Rather, nucleation occurs on the

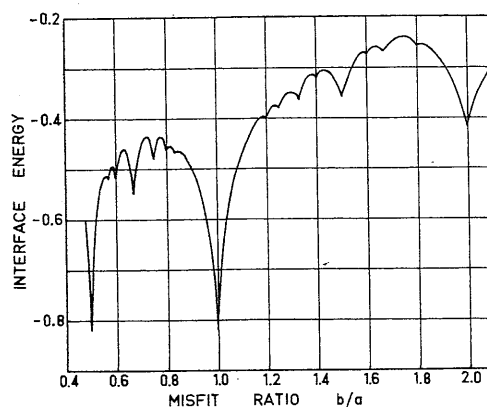


Fig. 5. Calculated interfacial energy for a one-dimensional interface between two simple crystals of lattice parameters a and b respectively [13].

relatively strain-free growth steps at some distance from the dislocation line itself.

The orientation of growing crystals parallel to particular crystallographic directions in the substrate is well known. A detailed understanding of the phenomenon requires a careful study of the atomic configuration and energy of the interface between two differing crystals. Work along these lines has been done by van der Merwe [11, 12] and more recently by the present author [13].

The growing embryo and substrate may differ from one another in both symmetry and lattice spacing and the variety of possible combinations is immense. For given embryo and substrate planes, however, there will be certain configurations which correspond to minima in the interfacial energy between the embryo and the substrate and hence to maxima in the parameter m . Embryos growing close to these favoured orientations have a lower energy barrier to surmount in nucleation and so will predominate in the experimental situation.

The mathematics of the problem is complex, involving three dimensions, and, as yet, explicit calculations have been made only for

the case of the one-dimensional interface between two two-dimensional crystals. An example of the result of such a calculation is given in Fig. 5. This shows the energy per unit length of interface between two such crystals, having lattice parameters a and b respectively, on the assumption that the interaction potential between neighbouring atoms is parabolic. It can be seen that the energy has sharply cusped minima when the two lattice parameters are in simple ratio. The width of the cusps depends upon the elastic

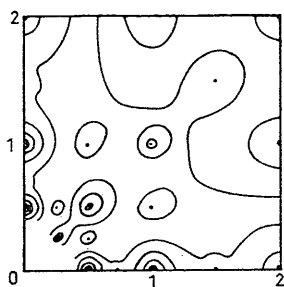


Fig. 6. Energy contour diagram for the energy of the interface between (100) planes of two simple cubic crystals.

constants of the crystals involved, which in this case follow simply from the assumed interaction potential.

Very much the same situation occurs in the real three-dimensional case except that relative orientation must now be considered as well as lattice parameter ratio. Fig. 6 shows the behaviour to be expected for two crystals of simple cubic structure making contact on (100) faces. The length of a radius vector from the origin gives the ratio of the lattice parameters of the two crystals and its orientation gives the angle between corresponding directions in the two lattices. The positions of the principal energy minima are shown and the contours give a qualitative indication of their relative depths. The square symmetry of the interface is clearly evident. For a given lattice ratio the depth and sharpness of possible energy minima determines the degree of coherence (in orientation) of the overgrowth crystals which are nucleated. Detailed calculations for this case have not yet been completed.

From studies of this kind it seems that it may be possible to calculate nucleation behaviour in simple cases from first principles.

Certainly some of the nuclei which are known to be effective for formation of ice crystals, such as silver iodide, have the right geometry to yield a low energy interface with ice in parallel orientation, while others, such as the newly investigated organic nuclei, are so soft physically that the energy cusps must be very broad. Better understanding should follow when interface energies for some of these materials have been calculated in detail.

4. DISCUSSION

In this brief review some of the work on nucleation of ice crystals which is most likely to be applicable to metallurgical problems has been mentioned. The study of ice itself is rather more complicated than would appear from this review and account must be taken of the configurational entropy of its crystal structure [14], the possibility that its free surface has a quasi-liquid structure [15] and the manifold problems associated with adsorption of vapour molecules on the nucleating substrate [16]. These problems are of much less importance in understanding the solidification of metals, though it is perhaps true to say that they are replaced by others no less complex and challenging.

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