NUCLEATION AND GROWTH OF ICE CRYSTALS UPON CRYSTALLINE SUBSTRATES

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Summary

The importance of various surface imperfections in the nucleation of ice crystals is considered and it is concluded that dislocations are not preferred nucleation sites, whereas steps and re-entrant corners do encourage nucleation. Expressions are derived for the height of the free energy barrier in several important cases, and the retention of embryos under unsaturated conditions is discussed. Embryos initially grow by two-dimensional nucleation, but ultimately a dislocation growth mechanism becomes more important. There is not yet enough experimental evidence to decide upon the reality of the entropy effect previously proposed, which inhibits nucleation upon certain crystal faces.

I. INTRODUCTION

The basis of the theory of the nucleation of new phases was established long ago by Volmer and Weber (1925) and Becker and Döring (1935), and remains fundamentally unchanged today. Within a supersaturated vapour, or a supercooled liquid, there are transient groupings of molecules having the structure of the stable phase—liquid or solid as the case may be. Because of their surface free energy these embryos are unstable and are continually being created and destroyed by thermal fluctuations, in such a way that their numbers maintain a Boltzmann distribution in energy.

The free energy barrier associated with the formation of an embryo has a maximum value at a certain critical size. Smaller embryos tend to disappear, but once an embryo exceeds this critical size it can grow without limit. The probability of an embryo growing to critical size is a very sharp function of supersaturation or supercooling, so that the nucleation process has a sharp threshold which is relatively easy to determine experimentally.

Homogeneous nucleation within the pure substance itself presents a large free energy barrier, and requires supersaturations of hundreds of per cent. or supercoolings of many tens or even hundreds of degrees. The presence of foreign particles or surfaces lowers the barrier greatly and most phase transformations take place by such a process of heterogeneous nucleation.

The theory of homogeneous nucleation is by now fairly well developed, though on a molecular basis many of its concepts are rather unsatisfactory. Similarly, nucleation of crystals upon perfect crystalline substrates (Turnbull and Vonnegut 1952) and upon perfect spherical particles (Fletcher 1958) have

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been dealt with, at least to a first approximation. The purpose of the present paper is to discuss the role of surface imperfections in the substrate upon its efficiency as a nucleation catalyst. The particular case of conical pits in an otherwise flat surface has been considered by Turnbull (1950) on a non-crystalline approximation, but here we shall be concerned with such specifically crystalline structures as growth steps and dislocations.

II. Nucleation Theory

Before we consider the nucleation and growth of a crystal embryo on a substrate, we must make some detailed assumptions about the properties of this embryo, and in particular about its surface. The structure of a liquid surface is disordered, so that all surface orientations have the same free energy per unit area, and surface free energy will generally be minimized when the surface assumes the shape of a part of a sphere. The surface free energy of a crystal face, on the other hand, is strongly dependent upon the orientation of

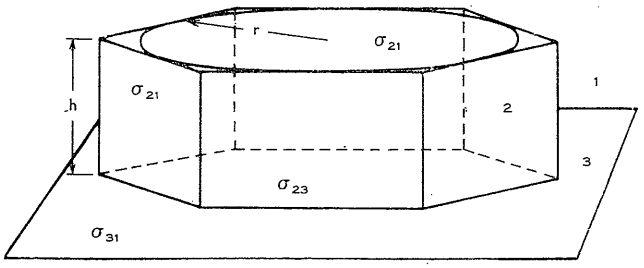

Fig. 1.—A prismatic embryo growing upon a perfect plane substrate. Subscript 1 refers to the parent phase, 2 to the embryo, and 3 to the substrate.

the face relative to the crystal axes. The surface free energy of a crystal will therefore generally be a minimum when the crystal has some typical polyhedral habit. Burton and Cabrera (1949) have discussed the structure of such habit faces in some detail and their results indicate that for many materials near room temperature these faces are, in equilibrium, almost atomically flat. Higher index faces, however, or even habit faces at higher temperatures may become rough on an atomic scale.

A crystalline embryo growing on a smooth substrate thus has the general appearance shown in Figure 1, which is drawn for the case of a crystal whose habit is a hexagonal prism. The geometry of such a prismatic embryo is characterized by its height h, the inscribed radius r, and the number n of prism faces.

If we define a parameter ξ by

$$\xi=(n/\pi)\tan(\pi/n), \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

then the free energy of formation of the embryo is

$$\begin{aligned}\Delta G &= (\text{volume free energy})+(\text{surface free energy})\\ &= \pi r^2\xi h\Delta G_v+\pi r^2\xi(\sigma_{23}-\sigma_{31})+(\pi r^2\xi+2\pi r\xi h)\sigma_{21}, \qquad \ldots. \quad (2)\end{aligned}$$

where ΔG_v is the free energy difference per unit volume of crystal between the parent phase and the new bulk crystalline phase, and σ is the interface free energy per unit area. Subscripts 1, 2, and 3 refer to parent phase (vapour or liquid), crystalline embryo phase, and substrate respectively. For the sake of simplicity we have assumed all habit faces of the embryo to have the same value of σ_{12}.

If we define a quantity γ, which essentially measures the disparity between the embryo and substrate, by

$$\gamma=(\sigma_{21}-\sigma_{31}+\sigma_{23})/\sigma_{21}, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

then (2) can be simplified to

$$\Delta G=\pi r^2\xi h\Delta G_v+\pi r^2\xi\gamma\sigma_{21}+2\pi r\xi h\sigma_{21}, \quad \ldots\ldots\ldots \quad (4)$$

and we shall henceforth simply use σ to mean σ_{21}.

In a supercooled or supersaturated parent phase ΔG_v is negative, while $0\leqslant\gamma\leqslant 2$. The value of ΔG initially increases with increasing r and h, but decreases again after a critical size is reached. To find this critical condition we require

$$\partial\Delta G/\partial h=0, \quad \partial\Delta G/\partial r=0. \quad \ldots\ldots\ldots\ldots\ldots \quad (5)$$

The first of these gives the critical radius

$$r^*=2\sigma/\Delta G_v, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

while the second gives the equilibrium habit

$$h=r\gamma. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

This second result could also have been obtained by use of Wulff's rule (Wulff 1901), which states that in equilibrium the perpendicular distance of any face from the centre of a crystal is proportional to its free energy per unit area.

Substitution of (6) and (7) into (4) leads to the result

$$\Delta G^*=4\pi\xi\sigma^3\gamma/\Delta G_v^2. \quad \ldots\ldots\ldots\ldots\ldots \quad (8)$$

Provided that the number of molecules associated into embryos is much less than the total number of molecules of parent phase in contact with the substrate, the number of critical embryos per unit area is given by Boltzmann's distribution law as

$$n\exp(-\Delta G^*/kT), \quad \ldots\ldots\ldots\ldots\ldots \quad (9)$$

where n is the number of parent phase molecules in contact with unit area of substrate. The rate at which critical embryos gain an additional molecule to become freely growing is the nucleation rate J and is given by

$$J=An\exp(-\Delta G^*/kT). \quad \ldots\ldots\ldots\ldots \quad (10)$$

The kinetic constant A depends upon details of the system considered.†

† Strictly speaking J should be an integral taking into account all possible ways of crossing the free energy barrier of which ΔG^* is the height of the saddle point. As far as the author is aware no detailed consideration has yet been given to this point, and all theories use a simple one-dimensional approximation as we have done here. It is possible that this consideration could make an order of magnitude difference to the rate J. In view of similar uncertainties in the quantity A, however, this is not of any practical importance in the present state of the theory.

For nucleation from a supersaturated vapour

$$A \sim 4\pi r^{*2} p/(2\pi mkT)^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

(Volmer and Weber 1925), where p is the partial pressure of the vapour and m the mass of a vapour molecule. A more exact expression for A has been given by Becker and Döring (1935) but this will not concern us here. The value of ΔG_v in this case can be written explicitly as

$$\Delta G_v = (-kT/V) \ln (p/p_\infty), \quad \ldots\ldots\ldots\ldots\ldots (12)$$

where V is the volume occupied by a molecule in the crystal, and p_∞ is the vapour pressure in equilibrium with a crystal of infinite extent.

For nucleation from a liquid the kinetic coefficient has been derived by Turnbull and Fisher (1949) to be

$$A \sim (kT/h) \exp (-\varphi/kT), \quad \ldots\ldots\ldots\ldots\ldots (13)$$

where φ is the activation energy for short-range diffusion in the liquid. In this case ΔG_v is given approximately by

$$\Delta G_v = -|\Delta S_v| \Delta T, \quad \ldots\ldots\ldots\ldots\ldots (14)$$

where ΔS_v is the entropy of fusion per unit volume of crystal and ΔT is the supercooling of the liquid.

In either case, for substances with fairly average properties the kinetic coefficient A is of order 10^{25} cm^{-2} sec^{-1}, an uncertainty of a few orders of magnitude having little effect since the behaviour of J is completely dominated by the exponential term in (**10**).

We have not, as yet, taken any account of the molecular nature of the crystal and substrate. This has been discussed by Turnbull and Vonnegut (1952), who show that two effects must be considered. In the first place, the interfacial free energy σ_{23} will depend upon the dislocation content of the interface, which in turn depends upon the relation between the crystal structures of embryo and substrate. This effect contributes to the value of γ and is automatically taken into account in our discussion. If, however, the structure and cell dimensions of the surfaces of substrate and embryo are very similar the interface may contain no dislocations, the misfit being taken up in elastic strain ε in the embryo. In this case a strain energy term of order $C\varepsilon^2$ must be added to ΔG_v as given by (**12**) or (**14**). This added term means that a larger supersaturation or supercooling is required for nucleation than would be the case if the embryo were unstrained. We shall mention this effect again later.

III. Nucleation on Dislocations

The first topic to be discussed is the role of dislocations as nucleation sites. Edge dislocations can be dismissed almost immediately, as they will, except in very special circumstances, merely contribute more dislocations to the interface, or elastic strain to the embryo. The case to be considered is that of a screw dislocation meeting an otherwise perfect face. An embryo growing on such a dislocation will suffer by reason of elastic strain, but will be able to add further molecular layers by the Frank mechanism (Frank 1949) instead of requiring surface nucleation. The question to be considered is whether the combined effect raises or lowers the effective ΔG^*.

The two possible situations are shown in Figure 2 where polygons have been replaced by circles for clarity. Figure 2 (*a*) shows a prismatic embryo with a single molecular layer or two-dimensional embryo growing on its upper surface, while Figure 2 (*b*) shows a dislocated embryo. It must be admitted that these pictures are not complete since they provide no mechanism for lateral growth of the embryo, but they do represent a closer approach to reality than the perfect embryo of Figure 1. It should be emphasized that the dimensions R and r are not necessarily equal in the two figures.

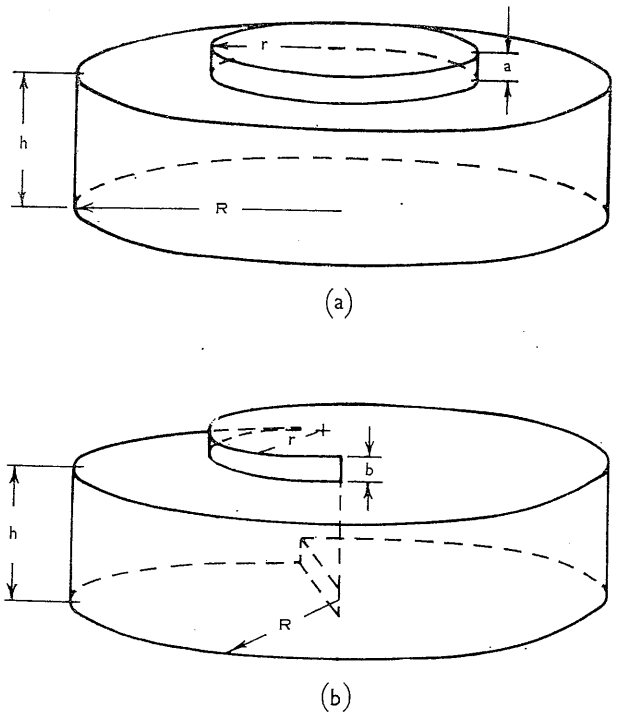

Fig. 2.—Crystalline embryos growing upon (*a*) a perfect substrate, and (*b*) a substrate from which emerges a screw dislocation with Burgers vector b.

The free energy of formation of these two structures can be written down analogously to equation (**2**). For the non-dislocated embryo we have

$$\Delta G_1=\pi R^2\xi h\Delta G_v+\pi R^2\xi\gamma\sigma+2\pi R\xi h\sigma+\pi r^2\xi a\Delta G_v+2\pi r\xi a\sigma, \quad \ldots\ldots\ldots \quad (15)$$

where a is the unit cell dimension along the axis normal to the substrate. For the dislocated embryo

$$\Delta G_2=\pi R^2\xi h\Delta G_v'+\pi R^2\xi\gamma\sigma+2\pi R\xi h\sigma+\tfrac{1}{2}\pi r^2\xi\Delta G_v'+\pi r\xi b\sigma+2rb(\gamma-1)\sigma, \quad (16)$$

where $\Delta G_v'$ includes the contribution of elastic strain energy and b is the Burgers vector of the dislocation.

When the critical values ΔG_1^* and ΔG_2^* are evaluated as before it is found that

$$r^*=\tfrac{1}{2}R^* \quad \ldots\ldots\ldots\ldots\ldots \quad (17)$$

as drawn, and that

$$\Delta G_1^* = \frac{4\pi\xi\sigma^3\gamma}{\Delta G_v^2} - \frac{\pi a\xi\sigma^2}{\Delta G_v}, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (18)$$

and

$$\Delta G_2^* = \frac{4\pi\xi\sigma^3\gamma}{\Delta G_v'^2} - \frac{\pi a\xi\sigma^2}{\Delta G_v'}\left(2\gamma - \frac{3}{2}\right). \quad \ldots\ldots\ldots \quad (19)$$

The second term in (**18**) is positive, whilst the second term in (**19**) is negative for small γ. However, since $|\Delta G_v'| < |\Delta G_v|$ the first term of (**19**) is larger than the corresponding term in (**18**) by an amount which can be found for specific cases.

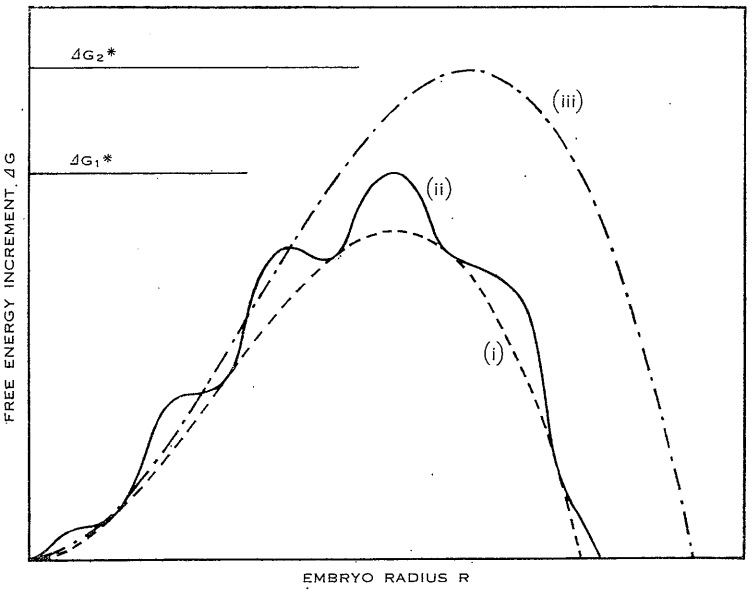

Fig. 3.—Free energy barrier to nucleation under various assumptions : (i) simple embryo with surface nucleation neglected ; (ii) simple embryo including surface nucleation, (iii) embryo containing a screw dislocation.

The situation is illustrated in Figure 3 where we have drawn curves of ΔG as a function of R for the simple case considered in Section II, for an embryo with surface nucleation, and for an embryo containing a screw dislocation. Whilst the dislocated embryo is presented with a simple nucleation barrier, the barrier for an embryo requiring surface nucleation is multiple. Such multiple barriers have been discussed by Giddings and Eyring (1958) who show that only barriers lying within about kT of ΔG^* need be considered, the kinetic coefficient A in (**10**) being divided by the number of barriers in this range. Typically $\Delta G^* \approx 60kT$ in this sort of nucleation process, and the total number of barriers (i.e. of molecular layers in the embryo) is usually of the order of ten. We can therefore neglect the multi-barrier aspect of the situation and consider simply the maximum height of the barrier.

Frank (1951) has considered the strain energy associated with screw dislocations in another connexion and we can use some of his results together with Penny's values for the elastic constants of ice (Penny 1948) to calculate this case. Frank gives the strain energy density as

$$\left.\begin{array}{ll} \mu b^2/8\pi r^2 & (r \geqslant 5b/\pi), \\ \mu b/20\pi r - \mu/200 & (r \leqslant 5b/\pi), \end{array}\right\} \quad \ldots\ldots\ldots\ (20)$$

where μ is the modulus of rigidity, and we shall take the Burgers vector b equal to the lattice constant along the z-axis.

The result for ice is that nucleation upon dislocations is impossible at temperatures above about -2 °C, and even at -20 °C dislocations are favoured nucleation sites only if $\gamma < 0 \cdot 005$. The situation is likely to be similar in most other materials, since according to Frank σ/μ does not vary widely, and it is essentially this ratio which determines the relative importance of surface and elastic energies.

We may thus dismiss dislocations as favoured nucleation sites, and in the next section we shall consider some other types of surface imperfections.

IV. Nucleation in Steps and Corners

The nucleation of crystals in steps or re-entrant corners of a substrate is most simply considered for the case of a hypothetical simple cubic crystal in which interactions are with nearest neighbours only. For such a crystal only {100} habit faces will even exist under equilibrium conditions, a {110} face, for example, being stepped on an atomic scale and having a surface free energy per unit area equal to $\sqrt{2}$ times that of a {100} face.

We shall consider only right-angled steps and corners, as shown in Figure 4, the contact constant being γ on all interfaces. The theory is developed exactly as in Section II of this paper, except that it is convenient to work in terms of the lengths of the three independent edges of the embryo, rather than in terms of an inscribed radius. The result in this case is particularly simple, the critical free energy being

$$\Delta G^* = \frac{32\sigma^3}{\Delta G_v^2}\left(\frac{\gamma}{2}\right)^n, \quad \ldots\ldots\ldots\ (21)$$

where n is the number of planes with which the embryo is in contact ($n=0$, 1, 2, or 3).

Since for almost any surface $\gamma < 2$, it is clear that corners ($n=3$) and steps ($n=2$) provide sites at which crystals can nucleate much more readily than upon a flat surface.

Equation (21) actually represents a simplification in that the two-dimensional nucleation which we considered in Section III has been neglected. This involves neglect of a term like the second in equation (18) and is not serious unless γ is small. When γ becomes zero, however, representing nucleation upon a substrate of the same material, the effect of this neglected term is important, as is manifest in the theory of crystal growth.

Another interesting point is that even in a corner and for $\gamma \ll 1$ there is a finite barrier to nucleation, and a finite supersaturation or supercooling is required to form a stable embryo. This is a consequence of the regularity of the crystal lattice and the assumption of only nearest neighbour interactions. These work to preclude the formation of non-habit faces of sufficiently low energy to provide a stable corner embryo in unsaturated conditions. This contrasts with the case of a liquid surface where all surface orientations have the same energy, so that a liquid corner embryo with concave surface can be stable below the saturation point. It is to be expected that the inclusion of second neighbour interactions might relax this effect.*

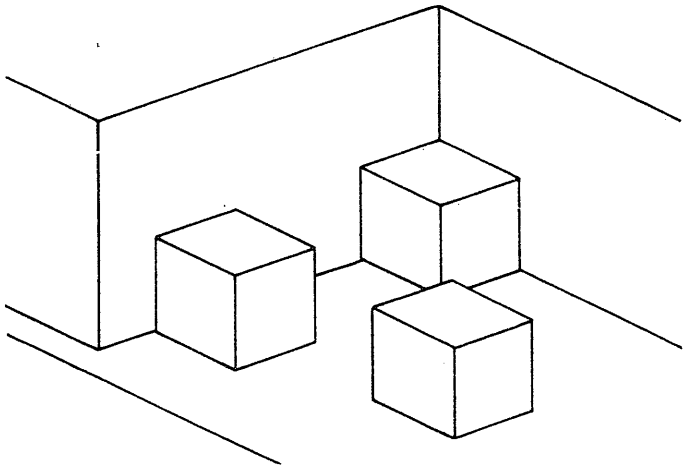

Fig. 4.—Nucleation of a simple cubic embryo on a plane surface, at a step, and in a corner.

Since we are concerned here principally with the case of ice we shall give results similar to equations (22)–(24) for a hexagonal lattice. The geometry is here rather more complicated, and Wulff's rule is useful in deciding upon the shape of the embryo. The general result is

$$\Delta G^* = \frac{16\sqrt{3}\cdot\sigma^3}{\Delta G_v^2} \cdot f(\gamma), \quad \ldots\ldots\ldots\ldots \quad (22)$$

where $f(\gamma)$ depends upon the geometry as shown in Table 1. Again the surface nucleation term has been neglected.

These results are less simple than in the cubic case, but the middle row of the table shows the same sort of behaviour as shown by equation (21). In the case of nucleation involving two prism faces meeting at an angle of $\pi/3$ a new phenomenon arises. The factor $f(\gamma)$ becomes zero for $\gamma = \frac{1}{2}$, and for such surfaces no supersaturation is required for nucleation in the edge or corner. If $\gamma < \frac{1}{2}$

* The substrate throughout has been considered to have the same habit faces as the embryo. If other faces occur on the substrate and produce a step, then it may become possible for an embryo to be retained on the step under unsaturated conditions, provided that the step angle is sufficiently small and the γ value low enough on the non-habit interfaces.

a change in the sign of ΔG_v is required for the critical embryo to exist, and this implies that a stable embryo can be retained in the edge or corner under unsaturated conditions.

It should perhaps be mentioned that no consideration has been given to the effect of any elastic strain energy caused by coherent growth upon the substrate. The contribution of this effect becomes increasingly serious when nucleation in steps or corners is considered, the strain energy being roughly proportional to the number of contact planes involved. We have, however, little knowledge of the extent to which such coherent growth occurs, and detailed consideration of particular cases would not be fruitful at this time.

TABLE 1

SHAPE FACTOR $f(\gamma)$ FOR VARIOUS SITUATIONS, FOR $\gamma \leqslant 1$

(Included angles are shown for prism faces)

Planes		Steps		Corners	
Free	1	Base-prism	$\gamma^2(2+\gamma)/12$		
Base	$\gamma/2$	Prism-prism $2\pi/3$	$\gamma^2/3$	$2\pi/3$	$\gamma^3/6$
Prism ..	$\gamma(2+\gamma)/6$	Prism-prism $\pi/3$	$(2\gamma-1)^2/6$	$\pi/3$	$\gamma(2\gamma-1)^2/12$

V. CRYSTAL GROWTH

We have as yet considered only the nucleation of a crystal embryo, and in the latter part of the discussion have neglected the necessity for nucleation of new crystal layers upon the growing embryo. We now return to this aspect of the problem and examine the course by which an embryo grows to a macroscopic crystal.

Reverting to the cubic crystal habit for simplicity, we recall that the free energy barrier to nucleation, at the intersection of n substrate planes, is

$$\Delta G^*_{[3]} = \frac{32\sigma^3}{\Delta G_v^2}\left(\frac{\gamma}{2}\right)^n. \qquad \ldots\ldots\ldots\ldots\ldots (23)$$

If now we examine the minimum free energy barrier to the formation of a two-dimensional embryo on top of such a three dimensional embryo, we find in a very similar manner

$$\Delta G^*_{[2]} = -\frac{4a\sigma^2}{\Delta G_v}\left(\frac{\gamma}{2}\right)^{n-1}, \qquad \ldots\ldots\ldots\ldots\ldots (24)$$

where a is the lattice spacing in the embryo. (This result holds if $n \geqslant 1$; if $n=0$, we must take $\gamma=2$.)

If then a three-dimensional embryo has nucleated, it will be able to grow freely by two-dimensional nucleation provided

$$\Delta G^*_{[2]} < \Delta G^*_{[3]}, \qquad \ldots\ldots\ldots\ldots\ldots (25)$$

which may be reduced to

$$-\Delta G_v < 4\sigma\gamma/a. \qquad \ldots\ldots\ldots\ldots\ldots (26)$$

The parameter γ has so far been considered to be entirely arbitrary within the range $0 \leqslant \gamma \leqslant 2$, but a little consideration shows that γ cannot in fact be made arbitrarily small, since the thickness of the embryo in any dimension must be at least equal to the lattice distance a. Equations (**6**) and (**7**) therefore lead to

$$h = -2\sigma\gamma/\Delta G_v \geqslant a, \quad \ldots\ldots\ldots\ldots \quad (27)$$

or

$$-\Delta G_v \leqslant 2\sigma\gamma/a. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (28)$$

If (**28**) is satisfied, as it must be, then (**26**) is automatically satisfied and the embryo can grow by two-dimensional nucleation of new crystal planes.

A growth mechanism such as this, however, becomes inactive when the value of $|\Delta G_v|$ has been decreased by diffusion of vapour to growing crystals. Crystals which contain screw dislocations require much lower supersaturations for appreciable growth to occur and will therefore grow at a much faster rate than undislocated embryos. In the absence of any other source of dislocations, embryos nucleated on substrate steps may grow slowly until they cross a screw dislocation in the substrate. This dislocation structure is then transferred to the growing crystal and further growth by the dislocation mechanism may proceed.

VI. Entropy Effect

Since we are applying our discussion to the nucleation of ice crystals, mention should be made of an effect suggested by the author (Fletcher 1959) which may have considerable influence on the nucleation efficiency of certain ionic substrates.

The dipoles of ice molecules normally have random orientations, even at absolute zero, so that ice has a residual entropy. If ice is caused to grow on an ionic substrate of which all the exposed ions are of one sign, then the configurational entropy of the ice molecules is greatly reduced and the free energy of the ice embryo increased.

This effect appears to be serious enough in the case of basal faces of substances like silver iodide and lead iodide to lower the threshold for the nucleation of freezing by about 30 °C and effectively render these faces inactive as nucleating agents. On the other hand the prism faces of these materials contain equal numbers of ions of each sign and after the first ice layer has grown the entropy has its normal value. We should thus expect these prism faces to provide the active nucleating sites.

Large steps on basal planes will, of course, expose prism faces, so that this theory, too, predicts that steps and corners on basal faces provide good nucleating sites, though for an entirely different reason.

VII. Experimental Results

Many observational studies have been made on the nucleation of ice crystals upon substrates of silver iodide or lead iodide. Among these should be mentioned the work of Jaffray and Montmory (1956, 1957), of Kleber and Weis (1958), and of Mason (1959); similar work has also been done by the present author.

The experiments all agree that steps in surfaces are preferred nucleation sites and that nucleation on perfect surfaces requires very large supersaturations or supercoolings. Mason reported that dislocations appeared to be good nuclea-

tion sites, but examination of his photographs shows relatively large pits around the dislocation site so that large steps were probably also available for nucleation.

Plate 1 shows the growth of ice crystals upon a substrate of lead iodide at −15 °C, growth taking place from a supersaturated vapour. It can be seen that steps provide numerous nucleation sites, the ice crystals near the centres of the terraces also appearing to be on steps rather than at the true centre where the dislocation line emerges. It should be noted that the steps in this photograph are of the order of a micron in height, so that they are of sufficient size for our theory to be applicable. Steps only a few molecular layers in height would require a different theoretical treatment.

It does not seem possible to decide on the basis of the experimental evidence whether the calculated entropy effect takes place or not. The results could be explained on the basis of operation of the entropy effect together with a small γ value, or of no entropy effect and a considerably larger value of γ. A decision on this point must await more definitive experiments.

VIII. Conclusions

We have seen how the classical theory of the nucleation of new phases on perfect substrates can be extended to discuss the effects of a variety of crystalline surface imperfections. Dislocations meeting the surface, whether of edge or screw character, do not ordinarily provide preferred nucleation sites, but steps and re-entrant corners are sites in which the free energy barrier to nucleation is greatly reduced.

An effect of this nature is to be expected by analogy with the nucleation of liquid droplets, but some of the features associated with the retention of liquid embryos in concave edges under unsaturated conditions do not apply fully to crystals. Crystals of hexagonal habit may, however, be retained in sufficiently sharp concave steps provided the interfacial free energy is small enough.

There is not yet sufficient evidence to allow a decision to be made on the reality of an entropy effect in ice crystal nucleation previously suggested by the author, but this does provide one of two alternate explanations of observed nucleation behaviour.

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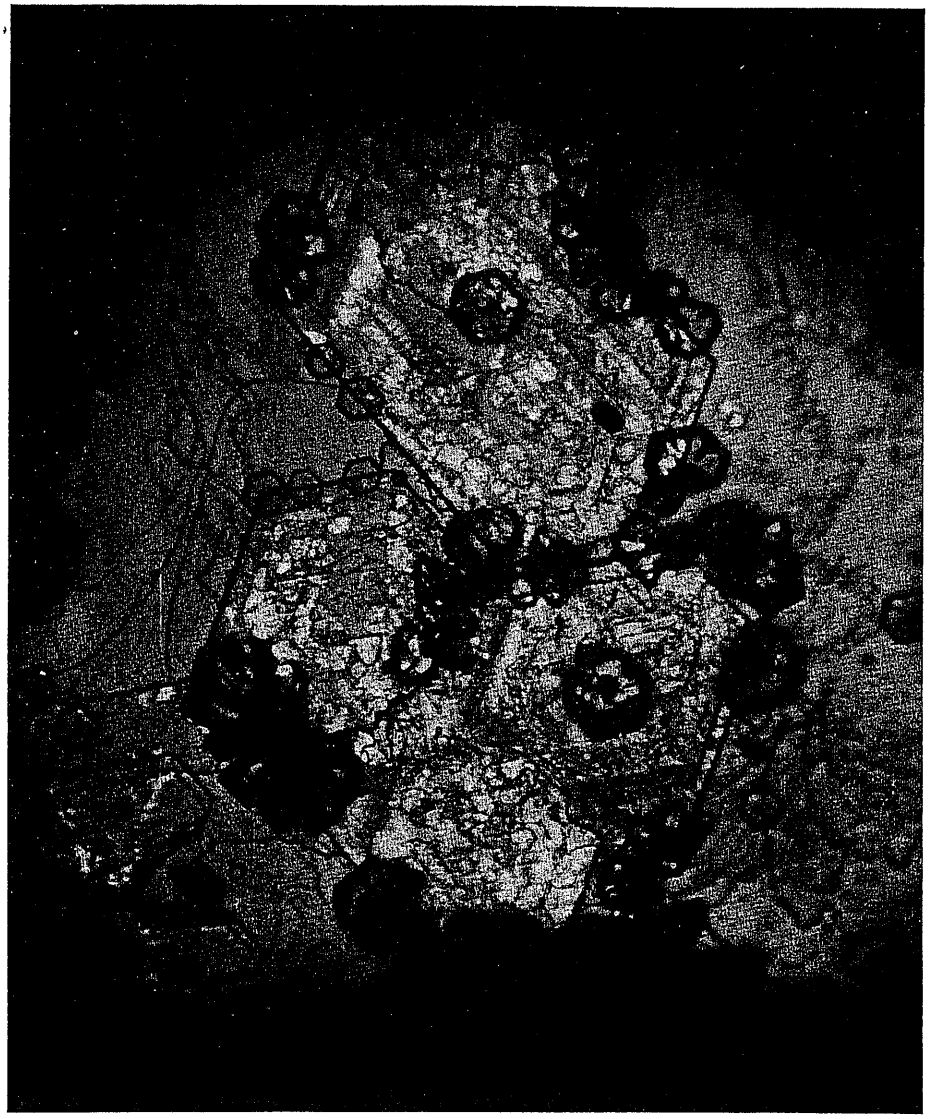

Nucleation of ice crystals from the vapour onto a lead iodide crystal substrate at about —15 °C.