

## Some Molecular Aspects of Ice Crystal Nucleation

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### 1. Introduction

The nucleation and growth of ice crystals from supersaturated vapour or super-cooled liquid phases are topics of considerable basic interest, as well as being of quite major importance in cloud physics. The crystallization process has, it is true, been studied in detail in many other systems, but it is in the water vapour-ice system that most attention has been paid to the detailed mechanism of nucleation.

Despite this concentrated study, however, many details of the nucleation process remain poorly understood. The general outlines of nucleation behaviour can, it is true, be very satisfactorily described by a sort of 'macroscopic' theory; but when microscopic details of molecular mechanism are investigated the single adjustable parameter of the macroscopic theory is found to cloak a good deal of uncertainty.

The present paper is concerned with a discussion of some molecular mechanisms in the nucleation process, particularly in the case of the water vapour-ice system.

### 2. Macroscopic Theory

What we have called the macroscopic theory of nucleation behaviour was developed some thirty years ago by VOLMER [1]<sup>2)</sup> and WEBER and subsequently refined by BECKER and DÖRING, and by ZELDOVICH and FRENKEL [2]. This theory assumes that macroscopic concepts, such as that of surface free energy, can be validly applied to very 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 thermodynamic, or better, by kinetic methods.

To illustrate this approach, consider a regular  $n$ -sided prism of the new phase 2 growing upon a plane substrate 3 in an environment 1. The free energy of formation of this embryo,  $\Delta G$ , depends on the interfacial free energies  $\sigma_{ij}$  and upon the free energy difference  $\Delta G_v$  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

$$\xi = \frac{n}{\pi} \tan \frac{\pi}{n} \quad (2)$$

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<sup>2)</sup> Numbers in brackets refer to References, page 495.

and the dimensions  $r$  and  $h$  are as shown in Figure 1. The expression for  $\Delta G$  is usually simplified by introducing the quantity  $m$  defined by

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

which specifies the degree of compatibility between the embryo and the substrate.

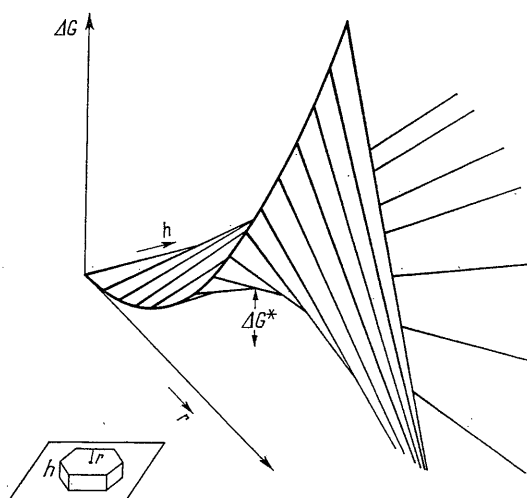


Figure 1

The free energy of formation,  $\Delta G$ , of a small prismatic embryo upon a nucleating substrate. The height of the free energy barrier to nucleation is  $\Delta G^*$ .

The form of the expression given for  $\Delta G$  is clearly that of a ruled surface, as is shown in Figure 1. 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  $\Delta G^*$ . This energy barrier is what limits the nucleation process, and the nucleation rate can be written [1, 2]

$$J = K \exp \frac{-\Delta G^*}{kT}, \quad (4)$$

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 curve of 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 has recently been treated by the present author [3]. 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

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

where  $\Delta G_0^*$  is the critical free energy for homogeneous nucleation,  $R$  is a characteristic dimension of the particle involved and  $m$  is given by (3). The forms of the function  $f$  for cases of interest, together with numerical calculations, have been given elsewhere [3].

When this theory is applied to various nucleation problems it is assumed that  $\sigma_{12}$  and  $\Delta G_0$  have their ordinary macroscopic values so that, assuming  $R$  to be known, the only adjustable parameter is  $m$ . It is found that in this form the theory gives a remarkably accurate description of the nucleation behaviour of silver iodide aerosols [4], and indeed apparently leaves very few results without adequate explanation. By a different appropriate choice of  $m$  the behaviour of most other nucleating materials can be similarly treated. Simple extensions also lead to quite satisfactory treatments of surfaces containing steps, dislocations and similar crystal features.

The success of this approach, however, tends to obscure the very considerable simplifications which have been made, in particular by introducing the quantity  $m$  which has, perforce, been treated as a parameter which can be assigned within reasonable limits. For the remainder of this paper we shall be concerned with some of the molecular interactions which have been compressed into this single parameter.

### 3. The Compatibility Parameter $m$

The parameter  $m$ , defined by Equation (3), is essentially a measure of the nucleation efficiency of a particular type of surface. In the simple case of the nucleation of liquid droplets from a vapour  $m$  is the cosine of the contact angle of the liquid on the substrate. From various arguments we can see that

$$-1 \leq m \leq 1. \quad (6)$$

A particle with  $m = 1$  is as efficient a nucleus as a particle of its size, shape and dislocation content can be. Effectively it behaves as an irreducible embryo of the new phase. On the other hand a surface for which  $m = -1$  is completely inactive in nucleation.

Evaluation of  $m$ , from (3), involves knowledge of three interfacial free energies— $\sigma_{23}$ , that of the interface between the embryo and the substrate;  $\sigma_{12}$ , that of the interface between the new phase and its parent phase; and finally  $\sigma_{13}$ , the free energy of the interface between the nucleating surface (which may be covered with an adsorbed layer) and the parent phase. We shall consider these in turn.

### 4. The Embryo-Substrate Interface

Several studies have been made of the free energy of the interface between embryo and substrate. Most of these treatments neglect entropy effects and so give free energy at 0° K or the energy component alone at a finite temperature. We shall come back to consider the entropy component later.

When two semi-infinite crystals meet in a plane interface it is possible, in principle, to compute the interfacial energy from a knowledge of atomic interaction potentials. In practice this has not yet proved possible, and it has been found necessary to

consider a very simplified form of interaction across the interface. In a plane parallel to the interface the potential can be written as a double Fourier series using the reciprocal vectors of the surface lattice. This potential may be investigated semi-quantitatively by retaining only the lowest Fourier components, and a further great simplification can be introduced by taking a plane section normal to the surface, thus yielding a one-dimensional interface.

The energy of such a one-dimensional interface has been considered by FRANK and VAN DER MERWE [5, 6]. They found that the energy of the interface depends quite critically upon the degree of misfit between the lattice parameters of the two materials and has a sharp minimum when these parameters are equal. This behaviour is due to the dislocation content of the interface, which increases smoothly with increasing misfit. Each dislocation introduces boundary energy and, in addition, elastic strain energy is stored in the bulk crystal close to the interface.

In the case where one of the crystals is reduced in thickness to a monomolecular layer, FRANK and VAN DER MERWE concluded that the equilibrium configuration might be one in which the epitaxial layer was uniformly constrained to conform with the substrate, the interface then containing no dislocations. They predicted this sort of behaviour for epitaxial layers of one or two molecules thickness and for misfits of less than about 10 per cent. SMOLLETT and BLACKMAN [7], however, argued that such uniformly strained layers are unstable and concluded that equilibrium layers will have, on the average, their natural lattice spacings.

The theory of FRANK and VAN DER MERWE in its simple form [5] which relates to a rigid substrate, has been applied to nucleation problems with some success by TURNBULL and VONNEGUT [8], though some of the numerical results are not consistent with the theory in absolute magnitude [9].

In extensions of this basic theory, VAN DER MERWE [6] has allowed for the fact that both the substrate and the overgrowth will suffer elastic distortions. The elastic energy is found to be stored in the two halves of the solid in inverse ratio to their shear moduli, a conclusion which may partially explain the results of NEWKIRK and TURNBULL [9] and which indicates in a general way that a good nucleating material should have a low shear modulus. This may be part of the reason why some organic materials, which should have a very small shear modulus on a molecular scale, are sometimes such efficient nuclei.

A further extension to the theory [6] treats the case of misorientation of the crystals about an axis normal to the interface. Again it was found that interfacial energy has a sharp minimum when the crystals are in parallel orientation—a result to be expected from numerous experimental observations of oriented overgrowths.

In some ways, however, the theory of FRANK and VAN DER MERWE is inadequate, and these inadequacies become quite important in many practical ice nucleation problems. The theory as presented is a solution of elastic strain equations, at the interface and in the bulk of the material, on the basis of an elastic stress function of particular form. A re-examination of the problem by means of a variational method shows that slightly more general assumptions are required if a true minimum is to be found for the interfacial energy. An investigation along these lines is now in progress and it is hoped to report results for several important interface problems at a later date. Meanwhile, however, a preliminary discussion of the one-dimensional case may

be of interest because it reveals important subsidiary energy minima (for example at lattice misfits of 2:1 and 3:2) which are important in nucleation problems.

Consider a one-dimensional substrate whose surface potential can be represented as a Fourier series

$$V(x) = - \sum_n V_n \cos \frac{2 \pi n x}{a}, \quad (7)$$

where  $a$  is the lattice spacing in the substrate. This series is not of the most general form, but will be adequate for the present discussion. Suppose the atomic positions  $x$  in the overlying layer are given by

$$x = m b + c, \quad m = 0, 1, 2, \dots, \quad (8)$$

where  $c$  is a displacement constant, and the lattice parameter  $b$  of the overlay is related to that of the substrate by

$$M b = N a, \quad (9)$$

$M$  and  $N$  being integers with no common factor. Then the average potential per atom of the overlay, without allowing any elastic distortion, is

$$E_1 = -\frac{1}{M} \sum_{m=1}^M \sum_n V_n \cos 2 \pi \left( \frac{m n N}{M} + \frac{n c}{a} \right). \quad (10)$$

The only terms remaining after the sum over  $m$  has been carried out are those for which  $nN/M$  is an integer, i.e.

$$n = s M, \quad s = 1, 2, \dots \quad (11)$$

Each such term contributes an energy  $-V_n \cos (2 \pi n c/a)$  and the displacement  $c$  can be chosen to minimize this total energy. The minimum so obtained will be at least as low as the result for a particular choice of  $c$  such as  $a/M$  or  $a/2 M$ . These two choices give respectively

$$E'_1 = - \sum_s V_{sM} \quad (12)$$

and

$$E''_1 = - \sum_s (-1)^s V_{sM} \quad (13)$$

and we may choose the lower of these two as a good approximation to  $E_1$ .

To a first approximation the substrate atoms may be treated on the assumption that the overlay potential is similar to that of the substrate except for a scale factor. The analysis is then similar and, in virtue of (9), the relative displacement  $c$  is the same as for the overlay, giving

$$E_2 = \min \left\{ - \sum_s V_{sN}, - \sum_s (-1)^s V_{sN} \right\}, \quad (14)$$

the same series being taken as for  $E_1$ . The total interfacial misfit energy is thus essentially

$$E \approx \frac{M E_1 + N E_2}{M + N}. \quad (15)$$

Since the Fourier components  $V_n$  may be expected to fall quite sharply with increasing  $n$ , this analysis shows that one may expect subsidiary energy minima at lattice misfits which are related by small integers as in (9). When the effects of elastic strain are included, as in the analysis of VAN DER MERWE [6], all the energy minima may be expected to have finite width.

This overall behaviour is shown in a semi-quantitative way in Figure 2, which has been drawn for the case of a parabolic interatomic potential. The Fourier components here have the form

$$V_n = (-1)^{n+1} n^{-2} V. \quad (16)$$

Some broadening of the minima has been indicated qualitatively, but this has not been calculated.

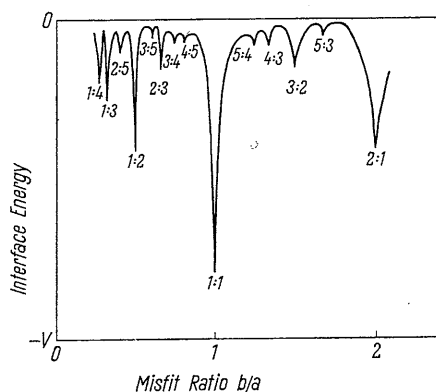


Figure 2

The energy of a one-dimensional interface between two crystals, having lattice parameters  $a$  and  $b$  respectively, when the lattice potential is assumed to be parabolic. Only the depths of the minima have been calculated; their widths are approximated from elastic considerations.

It can be seen that, in addition to the primary minimum for 1:1 fit, there are important subsidiary minima when the misfit ratio is simple, in agreement with the expectations aroused by nucleation experiments. It is to be expected that more detailed and rigorous analysis will confirm these findings.

It is also clear that it is not only the fundamental Fourier coefficient which is important, but also higher order coefficients, and these are specially important when the misfit is not 1:1. Putting this in physical terms, it is not merely the lattice geometry which affects the nucleation behaviour of a substrate but also the detailed nature of its surface potential and hence of its molecular binding.

### 5. Entropy Considerations

As was remarked earlier, a study like that above gives a value for interfacial energy rather than free energy. Since it is this latter quantity which is involved in the nucleation equations, the entropy term must be evaluated and explicitly included.

For many solids the entropy term may not be of particular importance, but this is not so in the case of ice nucleation. Each water molecule is a dipole which, in an ice

structure, has a certain number of possible orientations all of which contribute to the configurational entropy. If the surface of the substrate is such as to decrease this configurational freedom, then the free energy will be correspondingly raised. Again in the case of ice this entropy defect may be carried into the bulk of the material rather than be localized at the interface, thus leading to correspondingly increased effects.

This problem has been discussed by the present author [10] with the conclusion that substrate faces exposing ions of one sign only should be poor nuclei while faces exposing equal numbers of positive and negative ions should show no such inhibition. In the case of pure silver iodide this implies that entropy effects should inhibit nucleation on basal faces, while prism faces should be unaffected.

EDWARDS and EVANS [11] have pointed out that the influence of adsorbed  $\text{Ag}^+$ - or  $\text{I}^-$ -ions should appreciably alter this behaviour, and have found a maximum in the activity of silver iodide particles prepared from suspensions near the isoelectric point, in substantial agreement with the theory.

If a criterion of minimum entropy deficit were to be used in a search for new ice nuclei, then one might favour materials with exposed OH-groups of suitable geometry. This may again partly explain the activity of certain organic materials. Alternately one might seek for more or less ionic materials whose faces expose equal numbers of positive and negative ions, again with suitable geometry.

## 6. Surface of the Embryo

Relatively little attention has been paid in the literature to the free energy of the surface which the embryo presents to its parent phase. In the case of a liquid embryo it has been customary to use the macroscopic surface tension, with perhaps a small and rather uncertain correction for curvature in very small embryos. For solid-vapour interfaces experimental values for surface free energies are scarce and theoretical estimates rather uncertain, though usually sufficient to give satisfactory agreement with nucleation experiments<sup>3</sup>). The numerical magnitudes are even more uncertain for solid-liquid interfaces.

This analysis however neglects an important possibility, namely that the surface zone of the embryo may be of appreciable thickness. A structure of this type has long been under discussion in the case of ice, and recent semi-quantitative arguments [12] suggest that the surface zone of ice may have a disordered, quasi-liquid structure and a thickness of perhaps ten molecular layers at temperatures down to  $-10^\circ\text{C}$  or so.

Direct experimental evidence for such a surface structure is difficult to obtain; however, measurements of surface diffusion and surface conductivity on ice support the model in a general way. Recent nuclear magnetic resonance experiments by BARNES and SÄNGER [13] on the solidification of water adsorbed on silver iodide and similar materials also suggest a gradual phase change which is consistent with the existence of a surface transition layer.

<sup>3</sup>) It is sometimes said that nucleation experiments depend critically on this surface free energy. While this is true of the nucleation rate, this is not the quantity which is determined experimentally. Experiments almost invariably measure the threshold supersaturation or supercooling at which the nucleation rate reaches a particular value. This experimental quantity varies only as the three-halves power of the surface free energy.

If such a surface zone does exist in ice then it may have two important effects. In the first place it admits the possibility that the surface free energy of ice may vary quite rapidly with temperature in the vicinity of the melting point. Secondly it is clear that the transition zone may make up a considerable fraction of the total volume of the embryo and may be affected to some extent by the substrate. It is, perhaps, too early to consider these possibilities in detail, but they should not be lost sight of.

### 7. Surface of the Substrate

In any nucleation situation the surface of the substrate is clearly in a very complicated state, since it is on this surface that the whole population of embryos envisaged in nucleation theory develops. Ordinary adsorption theory is not adequate to treat this case since it is essentially an equilibrium theory, and in a supersaturated state true equilibrium cannot be attained and the amount of adsorbate becomes infinite. What must be developed instead is a time-dependent adsorption theory which is closely integrated with nucleation theory itself.

Whilst no such theory has yet been put forward, it is possible to see the lines upon which it might develop. If we consider a material such as silver iodide then it is known that the equilibrium adsorption of water vapour under unsaturated conditions is much less than a monolayer [14]. It is thus reasonable to assume, from the usual kinetic arguments, that the equilibrium amount of water adsorbed as single molecules is approximately proportional to the saturation ratio  $s = p/p_0$ , and that this equilibrium amount of adsorption will be essentially achieved after a very small time lag.

As well as this, however, the adsorbed molecules may exist in the form of clusters which are the sub-critical embryos of nucleation theory. The additional amount of material present in this form must be included in a count of all the adsorbate, and the time lag for the formation of the clusters must be allowed for when conditions are not those of equilibrium.

On a plane substrate with surface parameter  $m$ , which we use for simplicity though recognizing that it must depend on the adsorption conditions, the free energy excess  $\Delta G(n)$  of an embryo of  $n$  molecules is easily calculated. Under unsaturated conditions an equilibrium distribution of such embryos will be eventually attained, and the total adsorption at a saturation ratio  $s$  is approximately

$$N \approx A s \sum_n n \exp \frac{-\Delta G(n)}{kT}, \quad (17)$$

where  $A$  is a constant determined by the adsorption energy of single molecules on the substrate. This isotherm, which is the limiting form shown in Figure 3, resembles an ordinary Type III adsorption isotherm, though with finite adsorption at saturation.

When the environment is supersaturated the adsorption is time-dependent and depends in addition upon the adsorption history of the sample. It is possible to evaluate roughly the maximum adsorption possible before nucleation takes place by truncating the series in (17) above at the value of  $n$  corresponding to a critical embryo, for which  $\Delta G(n)$  is a maximum. The curve so obtained is shown qualitatively as a broken line in Figure 3 for the case of a substrate with  $m < 1$ . Shown also on this figure are curves indicating qualitatively the amount of adsorption to be expected at times before nucleation takes place.



A proper treatment of this adsorption process, possibly along the lines suggested above, is clearly necessary before any good understanding of heterogeneous nucleation is possible.

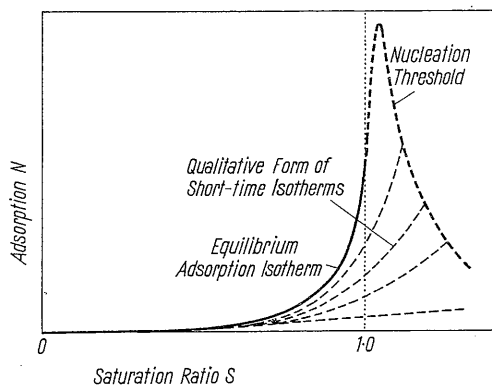


Figure 3

Time-dependent adsorption isotherms based upon the model discussed in the text.

## 8. Conclusions

It will be clear from the preceding discussion that a large number of phenomena on a molecular scale still remain to be investigated in detail in search of an understanding of nucleation processes.

In the first place energy and entropy considerations at interfaces and free surfaces need considerable study. Models with simply assigned interaction functions can provide useful information here, but ultimately calculations should involve the directional bondings found in ice and other molecular structures.

In addition the adsorption process under conditions of metastable equilibrium deserves close attention. Understanding of the mechanism of this process is closely linked with that of the whole nucleation problem.

## 9. Acknowledgment

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### Zusammenfassung

Der Vorgang der Keimbildung von Kristallen auf einer ebenen Unterlage wird auf molekularer Basis betrachtet. Hierzu wird über mehrere Ergebnisse eines neuartigen Annäherungsverfahrens berichtet. Man findet, dass die Energie, die einer eindimensionalen Grenzfläche zwischen zwei Kristallen zuzuordnen ist, Minima aufweist, wenn die Gitterkonstanten in einfachen Zahlenverhältnissen zueinander stehen. Die relativen Tiefen dieser Minima werden näherungsweise unter Annahme eines parabolischen Gitterpotentials berechnet. Ferner wird die metastabile Adsorption an einer keimbildenden Unterlage untersucht und hierfür ein neuartiges Modell für die Adsorptionsisotherme vorgeschlagen.

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## Ice Nucleation by Hydrophobic Substrates

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### Introduction

At the University of Arizona meeting on cloud seeding [1]<sup>4</sup>) we revealed that several silver iodide preparations exhibited specific nitrogen surface areas (BET) far in excess of the surface areas determined by water vapor adsorption. The nitrogen is adsorbed over the entire surface whereas the water is not. Therefore, silver iodide surface is largely hydrophobic. The curious long-standing, but unjoined, controversy between the cloud physicists on the one hand and the colloid chemists on the other was thereby settled [2]. For the former regarded silver iodide as being hydrophilic and epitaxial with ice in accord with the fairly close fit of their crystal parameters, whereas the latter regarded it as being hydrophobic because it flocculates and settles out of colloidal dispersion upon reduction of charged double layers. The historical conclusion reached by the colloid chemist was correct, but the argument employed was specious since the floccules simply settle out due to gravitational forces. HALL and TOMPKINS [3] recently confirmed the hydrophobic nature of silver iodide

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<sup>4</sup>) Numbers in brackets refer to References, page 502.