

Nucleation by Crystalline Particles*

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Classical nucleation theory is applied to the production of particles of a crystalline phase by growth upon small foreign particles. Various possible particle shapes are considered and general curves are derived which can be simply applied to a large variety of physical situations.

INTRODUCTION

THE heterogeneous nucleation of a new phase by foreign particles suspended in the parent phase is of practical importance in many fields. Particularly important is an understanding of the way in which the efficiency of these foreign nuclei depends upon their size, shape, and surface properties.

In an earlier discussion of this problem,¹ the present author considered the simple case in which both the nucleating particle and the embryo of the new phase growing upon it were spherical in shape. The results of this treatment have proved useful in understanding the behavior of aerosols of silver iodide in the nucleation of ice crystals in the atmosphere,² as well as having application to other systems.

It is clear, however, that many nucleating particles cannot be regarded as even approximately spherical, and, in cases where the embryo of the new phase is crystalline, it too may depart significantly from the spherical approximation. It will be our purpose then, in the present paper, to consider the nucleation behavior of particles ranging in shape from disks to needles, and to take some account of the crystalline nature of the new phase. On the basis of results for such extreme cases it should be possible, by interpolation, to arrive at semiquantitative conclusions for nuclei and embryos of intermediate habits.

Whilst it is simplest to arrive at results for a particular substance whose physical properties are known explicitly, it is possible, with little sacrifice, to derive general results in terms of parameters which differ from one substance to another. Our discussion is therefore quite general, within the range of validity of certain assumptions which are later made explicit.

CLASSICAL NUCLEATION THEORY

Classical nucleation theory, as developed by Volmer and others,³ applies statistical arguments to the

probability of growth of an embryo of a new phase from a metastable environment. The rate J of nucleation of isolated elements of the new phase is given by an expression of the form

$$J = K \exp(-\Delta G^*/kT), \quad (1)$$

where ΔG^* is the free energy required for the formation of a single embryo of such a size that it is in unstable equilibrium with its environment, and K is a constant which is determined by the kinetics of the situation.

K can usually be determined, in order of magnitude, by relatively simple arguments,³ though many refinements are possible. Most interest, and most uncertainty, centers on the evaluation of ΔG^* . It is usual here to apply macroscopic concepts like surface free energy rather freely to discussions of molecular groupings of quite small size. This procedure is of very marginal validity in many cases, but it is still used because the results obtained by such methods agree quite well with experiment in cases where they have been checked,^{3,4} and because a more realistic molecular approach seems at present prohibitively difficult.

We consider, then, an embryo of the new phase 2 growing on a nucleating particle 3 within the parent phase 1. If V_2 is the volume of the embryo and S_{ij} is the area of the ij interface, then the free energy involved in forming this embryo is

$$\Delta G = \Delta G_v V_2 + \sigma_{12} S_{12} + (\sigma_{23} - \sigma_{13}) S_{23}, \quad (2)$$

where ΔG_v is the free energy required to form unit volume of phase 2 from phase 1 and σ_{ij} is the free energy per unit area of the ij interface. It proves convenient to introduce the parameter m , defined by

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

to express the degree of compatibility between nucleus and embryo. It turns out that

$$-1 \leq m \leq 1, \quad (4)$$

with values of m approaching unity indicating a high degree of compatibility, analogous to "wetting" in the case of a liquid embryo.

Once the geometry has been made explicit so that V_2

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¹ N. H. Fletcher, *J. Chem. Phys.* **29**, 572 (1958); **31**, 1136 (1959).

² N. H. Fletcher, *J. Meteorology* **16**, 173, 249, 385 (1959), *Discussions Faraday Soc.* **30**, 39 (1960).

³ M. Volmer, *Kinetik der Phasenbildung* (Theodor Steinkopff Verlag, Dresden, 1939).

⁴ S. Twomey, *J. Chem. Phys.* **30**, 941 (1959).

and the S_{ij} are known, the maximum value of ΔG as a function of embryo size can be determined, and this is the quantity ΔG^* involved in Eq. (1).

The results of this procedure can be expressed in quite general form. Let R be some characteristic dimension of the nucleus, and r^* some characteristic dimension of the critical embryo which is in unstable equilibrium with its environment. Then if we define

$$x \equiv R/r^*, \quad (5)$$

we can write

$$\Delta G^* = \Delta G_0^* f(m, x), \quad (6)$$

where ΔG_0^* is the critical free energy for homogeneous nucleation in the absence of any foreign particle and $f(m, x)$ is a function whose form depends in detail upon the geometry of the situation.

For a spherical embryo

$$\Delta G_0^* = 16\pi\sigma_{12}^3/3(\Delta G_v)^2, \quad (7)$$

while for an n -sided prismatic embryo,⁵ assuming σ_{12} to be the same for all faces,

$$\Delta G_0^* = 8\pi\sigma_{12}^2\xi/(\Delta G_v)^2, \quad (8)$$

where

$$\xi = (n/\pi) \tan(\pi/n). \quad (9)$$

All this analysis neglects, to a large extent, the essential nature of a crystalline embryo. Thus, the dimensions of the embryo are considered to be continuously variable, and the two-dimensional nucleation of new molecular layers is neglected. In most cases this difficulty may be side-stepped by supposing the nucleus to contain a screw dislocation of small Burgers' vector, so that the embryo is similarly dislocated and two-dimensional nucleation is not required for growth. Detailed consideration of this point is complicated⁶ but it need not be discussed here. In the case of ice-crystal nucleation a possible anomalous surface structure⁷ may obviate the necessity for surface nucleation at the ice-vapor interface.

We assume in what follows that some such mechanism intervenes so that the expressions (6)–(9) are valid and the problem is essentially reduced to the geometrical one of evaluating $f(m, x)$.

GEOMETRICAL CONSIDERATIONS

Evaluation of the factor $f(m, x)$ for various geometries is straightforward though rather tedious. The methods involved have been described before.^{1,5} In the cases detailed below, the nucleus and embryo are considered either to be spherical, or to have the form of a circular cylinder. Various combinations of these forms are able to approximate most important nucleation situations. The neglect of other crystal faces does not have a large effect on the results and, in the case

of the embryo, the rounding-off of corners is physically justified by entropy considerations.⁸

Sphere on Sphere

This case was treated in an earlier publication,¹ and is included here for completeness. The geometrical factor $f(m, x)$ is here given by⁹

$$f(m, x) = \frac{1}{2} + \frac{1}{2}[(1-mx)/g]^3 + \frac{1}{2}x^3\{2-3[(x-m)/g]+[(x-m)/g]^3\} + \frac{3}{2}mx^2\{[(x-m)/g]-1\}, \quad (10)$$

where

$$g = (1+x^2-2mx)^{\frac{1}{2}}. \quad (11)$$

In this and the other cases we consider, both R and r^* are unambiguously defined as radii, and r^* is given by the relation

$$r^* = -2\sigma_{12}/\Delta G_v. \quad (12)$$

Cylinder on Sphere

In the case of a cylindrical embryo it is necessary to make some assumption about the relation between the free energies of different crystal faces. We here make the assumption that the free energies of base and cylinder faces are equal, so that the equilibrium habit of a small crystal is one in which the height equals the cylindrical diameter. Some such assumption is necessary if the calculation is to proceed, and this one appears to be reasonably realistic, extreme crystal habits not usually being the result of equilibrium processes.

For this case, then, we obtain the result

$$f(m, x) = 1 - mx^2(1-h) - \frac{1}{2}x^2(1-h^2) + \frac{1}{3}x^3(1-h)^2(2+h), \quad (13)$$

where

$$h = [(1-4mx+4x^2)^{\frac{1}{2}}-1]/2x. \quad (14)$$

This result is only valid if

$$h \geq (x^2-1)^{\frac{1}{2}}/x. \quad (15)$$

If the condition (15) is not fulfilled, which only occurs for $x \geq 1$, then $f(m, x)$ is given by

$$f(m, x) = \frac{1}{2} + \frac{2}{3}x^3 - mx^2 + \frac{1}{3}(x^2-1)^{\frac{1}{2}}(3mx-2x^2-1). \quad (16)$$

Cylinder on Disk

Nucleation upon a cylindrical nucleus is best considered through the two extreme cases in which the cylinder has the form either of a disk or of a needle.

⁵ N. H. Fletcher, Australian J. Phys. **13**, 408 (1960).

⁶ See reference 5, but note that the conclusion expressed in Sec. V is incorrect.

⁷ N. H. Fletcher, Phil. Mag. **7**, 255 (1962).

⁸ W. K. Burton, N. Cabrera, and F. C. Frank, Phil. Trans. Roy. Soc. (London) **A243**, 299 (1951).

⁹ Note that $f(m, x)$ as defined here differs by a factor $\frac{1}{2}$ from that used in reference 1.

For the case of a disk we find, if $x \leq 1$,

$$f(m, x) = 1 - \frac{1}{2}x(1+m), \quad (17)$$

while, if $x \geq 1$,

$$f(m, x) = (1-m)/2. \quad (18)$$

Cylinder on Cylinder

As the other extreme we consider nucleation upon the curved surface of a long, needlelike cylinder. Nucleation upon the flat ends of the cylinder can be treated using results (17) and (18) above. For the present case we find

$$f(m, x) = \pi^{-1}[\psi + x(x-2m)\phi + \frac{1}{2}\sin 2\psi - \frac{1}{2}x^2\sin 2\phi], \quad (19)$$

where¹⁰

$$\phi = \cos^{-1}[(x-m)/g], \quad (20)$$

$$\psi = \cos^{-1}[mx-1/g], \quad (21)$$

with

$$0 \leq (\phi, \psi) \leq \pi \quad (22)$$

and

$$g = (1+x^2-2mx)^{\frac{1}{2}}. \quad (23)$$

RESULTS IN GENERAL FORM

From the results of the preceding section and a knowledge of K , σ_{12} and the form of ΔG_v for a given system, it is possible to calculate the nucleation rate J as a function of supersaturation or supercooling. It is, however, more useful for our present purposes to make certain simplifying assumptions and approximations so that our results may be more generally applicable.

To this end we note that in many common nucleation situations, both in a vapor and a liquid environment, the kinetic constant in the rate equation (1) is of order of magnitude 10^{25} cm⁻² sec⁻¹. We further note that a change of a few orders of magnitude in the value of this constant can be compensated for by a change of only a few percent in the value of ΔG_v . Also, to a good approximation, the surface area of the nuclei we are considering is of order $10R^2$. We may thus write¹¹ for the constant K in Eq. (1)

$$K \sim 10^{26}R^2, \quad (24)$$

where R is measured in cm and the rate J is in nucleation events per nucleus per second.

We may now define an appreciable nucleation rate to be $J \sim 1$ sec⁻¹, and, using Eqs. (1), (6), and (8) for a cylindrical embryo, we find that for an appreciable nucleation rate

$$\Delta G_v^2 = 8\pi\sigma^3 f(m, x) / kT(60+2 \ln R), \quad (25)$$

where we have set $\xi=1$ and have written σ for σ_{12} .

¹⁰ ϕ and ψ are the angles so designated in figure similar to figure 1 of reference 1.

¹¹ If $x < 1$ it is better to write r^* for R in (24). We have done this in computing the curves shown later.

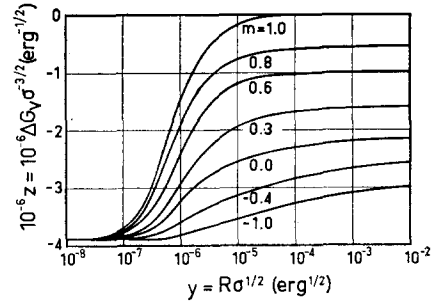


FIG. 1. General nucleation curves for the growth of an embryo of spherical habit upon a spherical nucleating particle. On each curve the nucleation rate is 1 particle⁻¹ sec⁻¹, z is proportional to supersaturation or supercooling, as given by (27), and y to particle radius, according to (28). Parameter m measures the compatibility of embryo and nucleus according to (3).

Using Eqs. (5) and (12), Eq. (25) can be put in the form

$$\frac{\Delta G_v^2}{\sigma^3} = \frac{8\pi f(m, -\frac{1}{2}R\sigma^{\frac{1}{2}}\Delta G_v/\sigma^{\frac{3}{2}})}{kT(60+2 \ln R\sigma^{\frac{1}{2}} - \ln \sigma)}. \quad (26)$$

If we now recognize that for most systems with which we deal, σ lies in the range 10–1000 erg cm⁻², we can write $\ln \sigma \approx 5$. This done, we can introduce the quantities

$$z \equiv \Delta G_v/\sigma^{\frac{3}{2}}, \quad (27)$$

$$y \equiv R\sigma^{\frac{1}{2}}, \quad (28)$$

and, taking $T \approx 300^\circ\text{K}$, we find

$$z^2 \approx \frac{3.0 \times 10^{14} f(m, -\frac{1}{2}yz)}{27 + \ln y}. \quad (29)$$

Similarly, for the case of a spherical embryo, using (7) instead of (8), we arrive at an equation differing from (29) only by the replacement of the factor 3.0×10^{14} on the right side by the value 2.0×10^{14} .

While an analytic solution of (29), giving z as a function of y with m a parameter, is not generally possible, it is quite simple to obtain a numerical solution by successive approximations. This has been done with the aid of a small computer, Sirius, and the results are shown in Figs. 1 to 4.

The curves are, in all cases, qualitatively similar, but interesting quantitative differences are apparent. Geometrically matching cases such as sphere-on-sphere or cylinder-on-cylinder, shown in Figs. 1 and 4, respectively, produce very similar curves, except that $|\Delta G_v|$ values are rather greater in the case of a cylindrical embryo. When the habits are not similar, however, as in the case of a cylinder growing on a sphere, the nucleation efficiency of quite large particles with m values near unity is very markedly reduced. This can be clearly seen in Fig. 2. The case of a cylindrical embryo growing on a flat nucleus, as shown in Fig. 3, is interesting for the flatness of the curves for $x > 1$ and the sharp decrease in nucleation efficiency for $x < 1$.

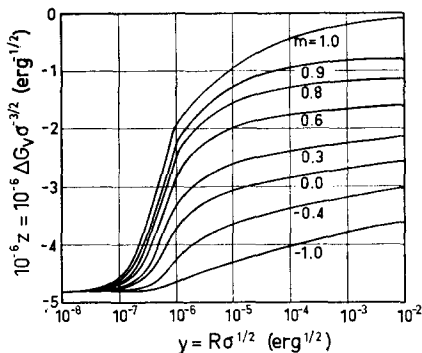


FIG. 2. General nucleation curves for the growth of an embryo of cylindrical habit upon a spherical particle.

USE OF THE GENERAL CURVES

As pointed out above, the curves given in Figs. 1 to 4 have been derived on the assumptions:

- (i) that the interfacial free energy σ_{12} lies in the range 10–1000 erg cm⁻²,
- (ii) that the kinetic constant K in Eq. (1) is of order 10²⁵ cm⁻² sec⁻¹,
- (iii) that an appreciable nucleation rate J is of order 1 particle⁻¹ sec⁻¹,
- (iv) that the temperature is near 300°K.

The curves should not be in error by more than about 10% on either axis for σ_{12} values in the stated range, for values of J or K differing by about three orders of magnitude from those given, and for temperatures in the range 250° to 350°K. For larger temperature variations the approximate relations

$$z(T) \approx (300/T)^{1/2} z(300^\circ), \tag{30}$$

$$y(T) \approx (T/300)^{1/2} y(300^\circ), \tag{31}$$

may be used as a guide to the results to be expected.

Providing these assumptions are reasonably valid, the general curves may be used to make predictions of nucleation behavior in a particular system by giving

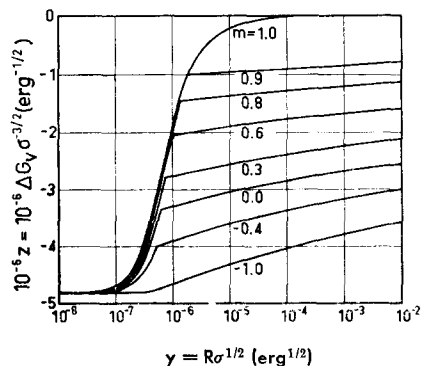


FIG. 3. General nucleation curves for the growth of an embryo of cylindrical habit upon a disk-shaped particle.

explicit forms to the parameters z and y defined in Eqs. (27) and (28).

The driving free energy per unit volume ΔG_v can be expressed in the general form

$$\Delta G_v = n(\mu_2 - \mu_1), \tag{32}$$

where μ_i is the chemical potential of molecules in phase i , and n is the number of molecules per unit volume in the condensed phase 2. For condensation or sublimation from a supersaturated vapor of pressure p

$$\Delta G_v = -nkT \ln(p/p_0), \tag{33}$$

where p_0 is the vapor pressure in equilibrium with a plane surface of the condensed phase. Similarly for

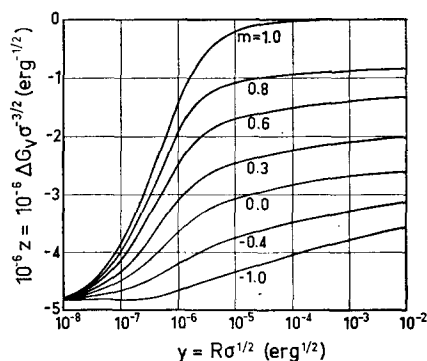


FIG. 4. General nucleation curves for the growth of an embryo of cylindrical habit upon the curved surface of a long needle-shaped particle.

crystallization of a solute from a solution in which its activity is a ,

$$\Delta G_v = -nkT \ln(a/a_0). \tag{34}$$

The remaining case of interest is the freezing of a pure liquid, for which

$$\Delta G_v \approx -\Delta S_v \Delta T, \tag{35}$$

where ΔS_v is the entropy of melting, per unit volume, and ΔT is the supercooling below the equilibrium freezing point.

CONCLUSION

We have derived general curves which may be used to make semiquantitative predictions about the behavior of small particles as heterogeneous nuclei for phase changes in various metastable systems.

The treatment is necessarily inexact because it is based upon the assumptions of classical nucleation theory, which neglects many molecular phenomena which may be of considerable importance. The success which has attended the application of even more simplified versions of this theory, however, allows one to hope that the present results will be a useful guide to average behavior in many common situations.