THEORY OF CRYSTAL GROWTH AND INTERFACE MOTION IN CRYSTALLINE MATERIALS*

JOHN W. CAHN†

The theory of crystal growth for diffuse and for non-singular surfaces is re-examined. It is found that if a critical driving force is exceeded the surface will be able to advance normal to itself without needing steps; if this driving force is not exceeded lateral step motion is necessary. For extremely diffuse interfaces this critical driving force will be so small that any measurable driving force will exceed it. For sharp interfaces the critical driving force will be very large, and most growth will occur by lateral step motion. For most systems however the critical driving force should be accessible experimentally.

In addition the nature of a step in a diffuse interface is discussed and its energy calculated. The conditions for interface motion by classical nucleation or screw dislocation mechanisms are derived.

THEORIE DE LA CROISSANCE DE CRISTAUX ET MOUVEMENT D'INTERFACE DANS DES MATERIAUX CRISTALLINS

La théorie de la croissance cristalline par des surfaces diffuses et sans singularité, a été réexaminée.

On a montré que si une force motrice critique est dépassée, la surface est apte à se mouvoir normalement à elle-même sans discontinuité.

Si la force motrice n'est atteinte, un mouvement discontinu latéral est nécessaire.

Pour des interfaces très diffuses, la force de mouvement critique peut être si faible que toute force motrice mesurable la dépassera.

Pour des interfaces nettes, la force motrice critique sera très grande et une croissance importante aura lieu par mouvement latéral discontinu. Pour la plupart des systèmes cependant la force motrice critique sera accessible experimentalement.

Enfin, la nature de la discontinuité dans une interface diffuse a été discutée et son énergie calculée.

Les conditions pour un mouvement d'interface par nucléation classique ou des mécanismes de dislocation-vis en ont été déduites.

THEORIE DES KRISTALLWACHSTUMS UND DER BEWEGUNG VON GRENZFLÄCHEN VON KRISTALLINEM MATERIAL

Die Theorie des Kristallwachstums für diffuse und nicht-singuläre Grenzflächen wird überprüft. Überschreitet die treibende Kraft einen kritischen Wert, so kann sich die Fläche in der Normalen-Richtung verschieben, ohne daß Stufen nötig sind. Für extrem diffuse Grenzflächen ist der kritische Wert so klein, daß jede meßbare treibende Kraft ihn überschreitet. Für scharfe Grenzflächen wird der kritische Wert der treibenden Kraft sehr groß sein, das Wachstum wird meist durch seitliche Bewegung von Stufen erfolgen. Für die meisten Systeme sollte die kritische treibende Kraft jedoch experimentell erreichbar sein.

Zusätzlich wird die Gestalt einer Stufe in einer diffusen Grenzfläche diskutiert und ihre Energie berechnet. Die Bedingungen für eine Bewegung der Grenzfläche durch klassische Keimbildung und einen Schraubenversetzungs-Mechanismus werden hergeleitet.

In the theory of crystal growth one distinguishes[1] between two major mechanisms:

(1) The surface advances by the lateral motion of steps one interplanar distance (or some integral multiple thereof) in height. An element of surface undergoes no change and does not advance normal to itself except during the passage of a step, and then it advances by the step height. It has been customary to assume the surfaces are sharp and that the steps have steep risers. We will here consider the step more generally as the transition between two adjacent regions of a surface, parallel to each other and identical in configuration, displaced from one another by an integral number of lattice planes. It is thus possible to conceive of a step in a diffuse surface even though the step height is much smaller than the thickness of the surface.

(2) The surface advances normal to itself without needing steps. This means that in the presence of a driving force every element of surface is capable of continued change leading to advance of the surface. For a sharp surface this continued change may be considered crystal growth by the more or less uniform change over large areas of each successive new layer to fit into the crystal whereas the growth of a diffuse surface requires simultaneous changes in several successive layers.

The distinction between these mechanisms is two-fold; one is geometrical–lateral motion of steps vs. motion of the whole surface normal to itself; the other based on the time sequence of an element of surface—no motion or change except when a step passes vs. continual change. We shall term the first

* Received November 9, 1959.

† General Electric Research Laboratory, Schenectady, New York.

mechanism nonuniform or lateral growth, and the second uniform or normal growth.

The prediction of which mechanism will be operative in a particular system is basic to the understanding of crystal growth. Two criteria have been used to make this prediction:

(1) The first is whether or not the surface is diffuse.[1,2] A diffuse surface is one in which the change from one phase to the other is gradual, occurring over several atom planes, and is in contrast to a sharp surface for which the major property change is confined to within one interplanar distance. The diffuse interface is thought to be able to advance normal to itself. What constitutes sufficient diffuseness and whether there is an abrupt transition from one mechanism to the other with increasing diffuseness has never been fully discussed.

(2) The other criterion is based on whether or not a surface is singular.[3,4] A singular surface is one for which the surface tension as a function of orientation has a pointed minimum. Growth of singular surfaces is known to require steps, whereas it is usually believed that non-singular surfaces can continuously advance normal to themselves.

The two criteria for the classification of systems according to expected growth mechanism have often been used interchangeably although they do not give identical answers. Furthermore, for either of the criteria the details for borderline cases have not been explored. It is for instance quite conceivable that a surface which is non-singular in the absence of a driving force could become singular when a driving force is applied.

The purpose of the present paper is to develop another criterion for classification. Consider the necessary requirements for the appearance of lateral growth. It is evident that the lateral growth mechanism will be found when any area in the surface can reach a metastable equilibrium configuration in the presence of the driving force. It will then tend to remain in such an equilibrium configuration until the passage of a step. Afterwards the configuration will be identical except that each part of the surface has advanced by the step height. If the surface cannot reach equilibrium in the presence of the driving force, then it will continue to advance without waiting for the lateral motion of steps.

The distinguishing feature is thus the ability of the surface to reach equilibrium in the presence of the driving force. In this paper we will therefore explore the nature of this equilibrium. The conclusion that is found is that, for every surface or interface in a crystalline medium, there exists a critical driving force, which, if exceeded, will enable the surface or interface to move normal to itself, and, if not exceeded, will require the lateral growth mechanism. This criterion, based on driving force will be compared with the other two criteria already described. Much of what will be discussed will apply not only to surfaces between a solid and a fluid, but also to interfaces in a crystalline medium when the same lattice extends into both phases as in order antiphase domain boundaries and ferromagnetic and ferroelectric domain walls.

In the next section we will examine the origin and magnitude of the minima that occur in the free energies of surfaces, interfaces and domain walls when these are in a crystalline medium. We shall find a lateral growth mechanism in all cases at sufficiently low driving force, and the details of this mechanism for diffuse interfaces will be explored in subsequent sections.

1. THE LATTICE RESISTANCE TO INTERFACE MOTION

In the absence of a driving force, an interface held parallel to a low index crystallographic plane will assume an equilibrium configuration. Because the interface is in a crystalline medium the identical configuration, displaced by an integral number of lattice planes, will also be an equilibrium configuration. We can conceive of the interface being forced to advance normal to itself. It can reassume the lowest free energy configuration only when it has advanced by an integral number of interplanar distances. All stages of intermediate advancement must correspond to configurations of higher free energy. In this section we will be concerned with this increase in free energy, which gives rise to a lattice resistance to the motion of the interface and results in a critical driving force necessary for the interface to advance uniformly normal to itself.

For a sharp interface these concepts are obvious, and it is generally accepted that lateral growth will persist until extremely high driving forces. The intermediate states of uniform advance may here be thought of as the various fractional coverages of one layer of atoms. One can conceive of the chemical potential necessary to maintain a given degree of coverage.[2] This chemical potential will reach some maximum value at some intermediate coverage and this maximum value defines the critical driving force, which is expected to be quite large.

For a diffuse interface there are many conceivable paths of advance from one equilibrium position to the next. We are aided by the fact that the path of interest to us proceeds over the lowest free energy barrier. This barrier, because it also represents an

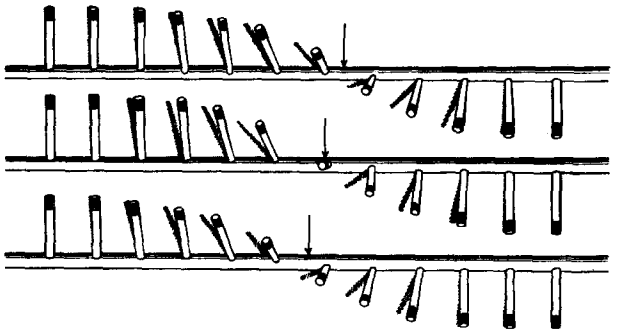

FIG. 1. Schematic drawing of a domain wall advancing. Each rod represents the direction of magnetization of a plane of atoms; each row of rods represents the domain wall at an instant of time. The arrow points to the center of the domain wall.

extremum in free energy (a saddlepoint), will also satisfy the same equilibrium equations which we use to obtain the equilibrium configuration. Fig. 1 illustrates schematically for a 180° magnetic domain wall two types of interface configurations each satisfying the conditions of equilibrium but differing in free energy. The domain wall with no spins in the hardest direction (i.e. symmetrical about an interstitial plane) is the lower in free energy.[5] Fig. 2 gives schematically the free energy as a function of position of the boundary.

We shall now concern ourselves with computing approximately the variation in free energy that an interface encounters as it is forced to advance uniformly through a crystalline medium in such a manner that the interface remains parallel to such a low index lattice plane.

We shall assume that the excess free energy F per unit area of interface in the absence of a driving force can be represented by a sum over the lattice plane of the form

$$F = a \sum_{n=-\infty}^{\infty} \{f(u_n) + Ka^{-2}(u_n - u_{n+1})^2\} \quad (1.1)$$
$$u_{-\infty} = u' \quad u_{\infty} = u'' \quad f(u') = f(u'') = 0$$

where u_n is some parameter which characterizes the nth lattice plane, u' and u'' the values of u in the two phases; a is the interplanar distance and K is a constant. For example u might represent the fraction of sites occupied, the composition, the angle which the magnetization makes with some specified direction or the degree of order. The function $f(u_n)$ represents the increase in free energy accompanying the creation of a unit volume of homogeneous material characterized by u_n from the materials reservoirs of the two bulk phases. The second term represents the additional work necessary to place such material in an environment of varying u_n and has been called the gradient energy.[6] In magnetic domain wall theory $f(u_n)$ is the crystal anisotropy energy and the second term is the exchange energy.[7] The extremals in F are obtained from the values of the u_n's given by a set of the difference equations

$$\frac{df}{du_n} + 2Ka^{-2}(2u_n - u_{n+1} - u_{n-1}) = 0. \quad (1.2)$$

Equation (1.2) may be substituted into equation (1.1) to give for the surface tension σ

$$\sigma = a \sum_n \left\{ f(u_n) - \tfrac{1}{2} u_n \frac{df}{du_n} \right\} \quad (1.3)$$

where the values of the u_n's must satisfy equation (1.2).

In general at least two sets of u_n's can be found, one corresponding to the surface tension of the equilibrium configuration, the other to the surface tension at the saddle. Because of the lattice structure, each set of u_n's is also a solution if each n is changed by an integer, corresponding to a translation of the surface by an integral number of lattice planes.

Sharp interfaces occur when the values of f for intermediate values of u are large compared to $Ka^{-2}(u' - u'')^2$. The solutions to equation (1.2) and hence σ are readily obtained. However for diffuse interfaces the solving of equation (1.2) represents considerable work, which can be reduced by an approximation which changes equation (1.2) into a differential equation.[6]

By changing the u's into a continuous variable of z, the distance normal to the boundary, we obtain for equation (1.2) the differential equation

$$\frac{\partial f}{\partial u} + 2K \frac{d^2u}{dz^2} = 0$$

which may be integrated to give

$$f = K\left(\frac{du}{dz}\right)^2$$

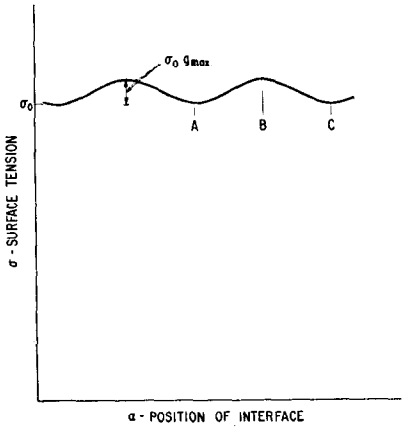

FIG. 2. The surface free energy of the domain wall of Fig. 1 as a function of its position. Minima correspond to configurations A and C, and maxima to B.

or

$$Z = \int_{u(0)}^{u(z)} \sqrt{(K/f)}\, du \tag{1.4}$$

in which u for $z = 0$ has been arbitrarily chosen.

In identifying the continuous variable $u(z)$ with the u_n's there is a certain arbitrariness in choosing the values of z corresponding to a lattice plane. Once the value of z for one lattice plane has been chosen the rest are determined. Let the value of z corresponding to the position of the 0th lattice plane be $-\alpha$. The quantity α thus gives the position of the interface relative to a fixed plane in the lattice.

Then

$$u_0 = u(-\alpha)$$

and

$$u_n = u(na - \alpha).$$

Using the method of Poisson sums* we are now in a position to evaluate the surface tension as a function of α from equation (1.3) and from the $u(z)$ obtained from a solution of equation (1.4).

$$\sigma = \int_{-\infty}^{+\infty} \left(f(u) - \tfrac{1}{2} u \frac{df}{du} \right) dz + 2 \sum_{s=1}^{\infty} \left[A_s \cos \frac{2\pi s\alpha}{a} - B_s \sin \frac{2\pi s\alpha}{a} \right] \tag{1.5}$$

where

$$A_s = \int_{-\infty}^{+\infty} \left(f(u) - \tfrac{1}{2} u \frac{df}{du} \right) \cos \frac{2\pi sz}{a}\, dz$$

$$B_s = \int_{-\infty}^{+\infty} \left(f(u) - \tfrac{1}{2} u \frac{df}{du} \right) \sin \frac{2\pi sz}{a}\, dz.$$

The first term is the value of the surface tension if one assumes the interface to be in continuous medium. The second term describes the periodic variation of the surface tension as the interface is made to move uniformly through the lattice, and constitutes the lattice resistance to the motion of the interface. The main assumption in deriving this term is that the interface is described by the same function $u(z)$ regardless of the value of α. This is probably a good assumption for diffuse interfaces.[9]

In order to obtain some feeling for the magnitude of the quantities let us assume that

$$f(u) = f_0(1 - u^2)^2$$

$$u' = -1 \qquad u'' = 1.$$

Then the solution to equation (1.4) is

$$u = \tanh \sqrt{(f_0/K)}\, z \tag{1.6}$$

and equation (1.5) gives

$$\sigma = \frac{8}{3} \sqrt{(Kf_0)} \left\{ 1 + \frac{2\pi^2 K^{\frac{1}{2}}}{a f_0^{\frac{1}{2}}} \sum_{s=1}^{\infty} s \left(1 - \frac{\pi^2 s^2 K}{2a^2 f_0} \right) \times \operatorname{cosech} \left(\frac{\pi^2 s}{a} \sqrt{\frac{K}{f_0}} \right) \cos \frac{2\pi s\alpha}{a} \right\}. \tag{1.7}$$

The quantity $n \equiv 2\sqrt{(K/f_0 a^2)}$ may be thought of as the thickness of the interface in numbers of lattice planes. For n large equation (1.7) reduces to

$$\sigma = \frac{8}{3} \sqrt{(Kf_0)} \left\{ 1 - \frac{\pi^4 n^3}{2^4} \exp\left(-\frac{\pi^2 n}{2} \right) \cos \frac{2\pi\alpha}{a} \right\} \tag{1.8}$$

which shows that σ rapidly becomes insensitive to the position of the interface as n becomes large. It

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* The Poisson sum formula[8] enables one to sum the values at periodic intervals of a function of a continuous variable

$$\sum_{n=-\infty}^{+\infty} y(na) = \frac{\sqrt{(2\pi)}}{a} \sum_{s=-\infty}^{+\infty} Y\left(\frac{2\pi s}{a}\right)$$

where $Y\left(\frac{2\pi s}{a}\right)$ is the Fourier cosine transform of y

$$Y\left(\frac{2\pi s}{a}\right) = \frac{1}{\sqrt{(2\pi)}} \int_{-\infty}^{+\infty} y(z) \cos \frac{2\pi z}{a}\, dz\,.$$

Since changing the sign of s does not affect the value of the Y's

$$\sum_{n=-\infty}^{n=\infty} y(na) = \frac{1}{a} \int_{-\infty}^{+\infty} y(z)\, dz + \frac{2\sqrt{(2\pi)}}{a} \sum_{s=1}^{\infty} Y\left(\frac{2\pi s}{a}\right).$$

The meaning of the Poisson sum formula is quite straightforward. Consider just the first two terms. We are trying to evaluate the sum of the values at periodic intervals of a function of a continuous variable. The integral of this function, the first term of the sum, is a first approximation, but it weighs all parts of the function equally heavily. The integral

$$\int_{-\infty}^{\infty} y(z) \cos \frac{2\pi z}{a}\, dz = \sqrt{(2\pi)}\, Y\left(\frac{2\pi}{a}\right)$$

tests whether the first term is a good approximation. It compares the value of y when z/a is close to being an integer with when it is not close to being an integer and makes a first approximation to the difference between the sum and the integral. The other terms represent higher correction terms.

The advantages of the Poisson sum method for this problem are the rapid convergence of the series for diffuse interfaces and also the ease with which the position α of the interface can be introduced. Consider the sum for various positions.

$$\sum_{n=-\infty}^{\infty} y(na - \alpha) = \frac{1}{a} \int_{-\infty}^{+\infty} y(z - \alpha)\, dz + \frac{2}{a} \sum_{s=1}^{\infty} \int_{-\infty}^{+\infty} y(z - \alpha) \cos \frac{2\pi sz}{a}\, dz$$

$$= \frac{1}{a} \int_{-\infty}^{\infty} y(z)\, dz + \frac{2\sqrt{(2\pi)}}{a} \sum_{s=1}^{\infty} \left(Y_{\cos}\left(\frac{2\pi s}{a}\right) \cos \frac{2\pi s\alpha}{a} - Y_{\sin}\left(\frac{2\pi s}{a}\right) \sin \frac{2\pi s\alpha}{a} \right)$$

where

$$Y_{\cos}\left(\frac{2\pi s}{a}\right) = \frac{1}{\sqrt{(2\pi)}} \int_{-\infty}^{+\infty} y(z) \cos \frac{2\pi sz}{a}\, dz$$

$$Y_{\sin}\left(\frac{2\pi s}{a}\right) = \frac{1}{\sqrt{(2\pi)}} \int_{-\infty}^{+\infty} y(z) \sin \frac{2\pi sz}{a}\, dz\,.$$

The periodic variation of the sum with α is thus conveniently expressed in terms of a Fourier series.

will be useful to introduce $g(\alpha) \geq 0$, a dimensionless periodic function of α defined by

$$\sigma(\alpha) = [1 + g(\alpha)]\sigma_0 \tag{1.9}$$

where σ_0 is the minimum value of σ as a function of α. The periodic part of σ is thus given by $\sigma_0 g(\alpha)$, and $g(\alpha)$ is the fractional change in surface tension from the equilibrium value for the position given by α. For that value of α, $g = 0$. The approximate equation (1.8) gives

$$g = \frac{\pi^4 n^3}{2^4} \exp\left(\frac{-\pi^2 n}{2}\right)\left(1 - \cos\frac{2\pi\alpha}{a}\right).$$

In the presence of a driving force the variation per unit area of surface in total free energy of a system due to uniform motion of the interface $\delta\alpha$ is approximately given by

$$\delta F = \left(\Delta F_v + \sigma_0 \frac{dg}{d\alpha}\right)\delta\alpha \tag{1.10}$$

where ΔF_v is the driving force, the change in free energy when the surface sweeps through a unit volume. The lateral growth mechanism is required only when there exists a value of α for which $\Delta F_v + \sigma_0(dg/d\alpha) = 0$. The maximum value of $\sigma_0(dg)/(d\alpha)$ for large n is given by $\pi\sigma_0 g_{\max}/a$. Hence

$$-\Delta F_v = \frac{\pi\sigma_0 g_{\max}}{a} \tag{1.11}$$

represents a driving force necessary to permit uniform advance of a diffuse interface. Such an advance does not need steps, and if in addition there are no diffusional barriers to motion, as in the case of a magnetic domain wall, the interface will be glissile, that is, it will be able to move without thermal activation. The free energy of the system as a function of interface position when the critical driving force is applied is shown in Fig. 3.

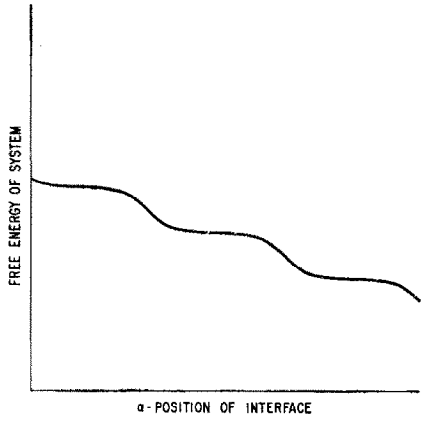

FIG. 3. The free energy of the system as a function of interface position when the critical driving force (equation 1.11) is applied.

Since the actual thickness of the diffuse interface is relatively insensitive to orientation[6] the thickness in terms of the number of lattice planes is inversely proportional to the interplanar distance a and hence directly proportional to the density of lattice sites. Thus the resistance to motion is greatest for close packed planes and zero for irrational index planes.

Although we derived $g(\alpha)$ as a function of interface thickness n for large n, the concept of $g(\alpha)$ is perfectly valid for sharp interfaces. It is possible to find a continuous function $u(z)$ in which the change from u' to u'' is confined to a distance of the order of one interplanar spacing which will adequately describe the surface at intermediate stages of uniform advance. For sharp interfaces the maximum value of $g(\alpha)$ can then be obtained directly from equation (1.1) and usually will be of the order of unity. This corresponds to a very high driving force.

At the other extreme we have the situation of a magnetic domain wall where n is of the order of one hundred. Here $g(\alpha)$ is so small that the critical driving force corresponds to undetectably small magnetic fields and any measurable driving force will exceed it. We thus find that for these extreme cases the criterion being developed in this paper agrees with the criterion based on diffuseness. But for systems having interfaces with intermediate degrees of diffuseness the critical driving force will be of measurable magnitude and both lateral and uniform growth should be observed.

It might be reasoned that when $g(\alpha)$ is sufficiently small the interface should be able to advance uniformly by thermal fluctuation. This is true if one considers a small enough area of the interface, but it is obvious that it cannot occur simultaneously over a large area. We thus are led naturally to a lateral mechanism, the mechanism of growth by two dimensional nucleation. We will next consider this mechanism and the other main mechanism of lateral growth, the screw dislocation mechanism. For both of these mechanisms we will first have to consider the nature of the step, the transition between two portions of the surface differing in degree of advancement.

2. THE FREE ENERGY OF A STEP IN A DIFFUSE INTERFACE

In the previous section it was shown that the interfacial free energy is a periodic function of the position of the interface relative to the lattice. The periodic part of the free energy becomes small compared to the surface tension as one considers more diffuse boundaries. This periodic energy represents a force tending to keep the interface

parallel to the low index crystallographic planes. It is well established that when a sharp interface is slightly inclined to a crystallographic direction, that the interface consists of large areas which follow the crystallographic direction and which are bounded by steps of height corresponding to an integral number of interplanar distances. In this section we will examine the nature and energy of the steps as we consider progressively more diffuse interfaces.

Consider an interface not quite parallel to a low index crystallographic plane. We may describe its position by giving α as a function of the x and y, the coordinates in the crystallographic plane. Then we can define the function L such that the excess free energy due the inclination of the surface is given by

$$\int\left\{g(\alpha)\sigma_0 + L\left[\left(\frac{\partial\alpha}{\partial x}\right)^2 + \left(\frac{\partial\alpha}{\partial y}\right)^2\right]\right\} dx\, dy\,. \qquad (2.1)$$

The first term represents the work (equation 1.9) to move the surface parallel to the low-index crystallographic plane to the position α, and the second term represents the work of inclining the surface from the low-index direction to the direction given by the x and y derivatives of α. The quantity L may be identified if we assume that $u(z)$ is independent of α and its derivatives. This gives

$$\left(\frac{\partial u}{\partial x}\right)^2 = \left(\frac{\partial u}{\partial z}\right)^2\left(\frac{\partial\alpha}{\partial x}\right)^2 \qquad (2.2)$$

$$\left(\frac{\partial u}{\partial y}\right)^2 = \left(\frac{\partial u}{\partial z}\right)^2\left(\frac{\partial\alpha}{\partial y}\right)^2.$$

For a cubic lattice and a scalar u

$$L\left[\left(\frac{\partial\alpha}{\partial x}\right)^2 + \left(\frac{\partial\alpha}{\partial y}\right)^2\right]dx\, dy = dx\, dy\int_{-\infty}^{+\infty} K\left[\left(\frac{\partial u}{\partial x}\right)^2 + \left(\frac{\partial u}{\partial y}\right)^2\right] dz$$

where K has the same meaning as in equation (1).

Combining equation (2.2) with the above, we obtain

$$L = \int K\left(\frac{\partial u}{\partial z}\right)^2 dz = \tfrac{1}{2}\sigma_0 \qquad (2.3)$$

which is the result one would have obtained if one noted that the surface energy per unit area in the continuum or cubic symmetry and scalar u is independent of orientation. If we now seek a minimum for equation (2.1) for the situation that $g = 0$ for $x = \pm\infty$ and $\alpha(+\infty) - \alpha(-\infty) = a$ we obtain that

$$\frac{1}{2}\left(\frac{d\alpha}{dx}\right)^2 = g(\alpha)$$

and that the excess energy ε per unit length of step is

$$\varepsilon = \sqrt{2}\sigma_0\int_0^a \sqrt{g}\, d\alpha \qquad (2.4)$$

or approximately

$$\frac{\varepsilon}{a\sigma_0} = \sqrt{g_{\max}}\,. \qquad (2.5)$$

One also may define a width of the step by

$$w = \frac{a}{\left(\frac{d\alpha}{dx}\right)_{\max}} = \frac{a}{\sqrt{g_{\max}}}\,. \qquad (2.6)$$

The value of w is expected to be very much larger than the thickness of the interface. This is not unreasonable even for a relatively sharp interface. For instance on a solid vapor surface it is calculated[1] that the equilibrium steps are quite ragged with jogs and holes extending over a number of atom distances, the width being greater, the greater is the equilibrium adsorption. It has usually been assumed that $\varepsilon/a\sigma_0 = 1$, but it is certainly always less than one and will be quite small for diffuse interfaces.

Since for small deviations from the crystallographic direction a surface can be represented by a series of steps, a knowledge of the step energy will enable one to derive the shape of the minima of the polar plot of the surface tension near the low angle crystallographic directions and from this shape it can be determined whether the surface can be considered singular or not.

If θ is the angle between the surface and a low index crystallographic direction and σ_0 the surface tension for a surface having the crystallographic direction then in a cubic material for θ large enough that the number of steps exceeds the intrinsic number due to thermal fluctuations.

$$\frac{\sigma}{\sigma_0} = 1 + \left(\frac{\varepsilon}{\sigma_0 a}\right)\theta = 1 + \sqrt{g_{\max}}\theta. \qquad (2.7)$$

3. THE THEORY OF GROWTH BY TWO DIMENSIONAL NUCLEATION

When the driving force for moving the surface is less than the critical driving force for uniform motion, the surface must advance by the motion of steps across the surface. In the absence of a screw dislocation terminating in the surface the steps are rapidly exhausted and the surface would become exactly parallel to the crystallographic plane, unless new steps can nucleate from thermal fluctuations which locally change the value of α. Classical nucleation theory considers an area of advance by one interplanar distance and surrounded by a closed step,

usually called a pillbox. The line tension of the step acts as force opposing the spreading of the pillbox and the pillbox will tend to disappear[10] unless

$$\frac{\varepsilon}{r} + a\Delta F_v < 0 \tag{3.1}$$

where r is the radius of the pillbox and ΔF_v is the driving force for the formation of the new phase.

The work W of forming a pillbox of critical radius r_c is

$$W = -\frac{\pi\varepsilon^2}{a\Delta F_v} \tag{3.2}$$

$$= \pi r_c \varepsilon \tag{3.3}$$

$$= -\frac{\pi}{2} r_c^2 a\Delta F_v \tag{3.4}$$

where

$$r_c = -\frac{\varepsilon}{a\Delta F_v}. \tag{3.5}$$

Because the step may be of considerable width these equations will lose their meaning if the critical radius becomes less than the width of a step. This condition gives

$$w < r_c = \frac{W}{\pi\varepsilon} \tag{3.6}$$

$$\frac{a}{\sqrt{g_{\max}}} < \frac{W}{\pi a\sigma_0\sqrt{g_{\max}}} \tag{3.6}$$

or

$$W > \pi a^2\sigma_0. \tag{3.7}$$

This condition automatically implies that

$$-\Delta F_v < \frac{\sigma_0 g_{\max}}{a} \tag{3.8}$$

or that the driving force is less, by a factor of π, than the critical driving force necessary for uniform motion (equation 1.10).

Growth by a two dimensional nucleation mechanism is expected to be measurable when W is less than 50 kT. We can therefore expect to observe growth occurring by classical two dimensional nucleation if

$$\pi a^2\sigma_0 < 50kT \tag{3.9}$$

and it will occur for a driving force less than $(\sigma_0 g_{\max})/a$. This condition for expecting a range of driving force in which observable growth by classical two dimensional nucleation is expected does not explicitly depend on the interface diffuseness.

If condition (3.8) is not met, that is, if the driving force is increased so that w is no longer less than the calculated radius of a classical nucleus then classical nucleation theory is not expected to hold. The critical nuclei are then given by particular saddle-points of the total free energy of the system as a function of $\alpha(x, y)$.

$$F = \int\left\{\alpha\Delta F_v + \sigma_0\left[1 + g(\alpha) + \tfrac{1}{2}\right.\right.$$
$$\left.\left. + \left(\left(\frac{d\alpha}{dx}\right)^2 + \left(\frac{d\alpha}{dy}\right)^2\right)\right]\right\} dx\, dy.$$

This equation is the two dimensional analogue of the equation used by Cahn and Hilliard[11] for three dimensional nucleation with $(\alpha\Delta F_v + \sigma_0 g)$ the two dimensional equivalent to their quantity f, and

$$\tfrac{1}{2}\sigma_0\left[\left(\frac{d\alpha}{dx}\right)^2 + \left(\frac{d\alpha}{dy}\right)^2\right]$$

equivalent to the gradient energy. Here critical driving force is equivalent to the spinodal and it is expected that the W will go to zero continuously as $-\Delta F_v$ approaches the critical driving force. The radius of the critical nucleus is expected to decrease with increasing driving force until it equals w and then is expected to become larger again, becoming infinite at the critical driving force. The maximum required change in α is expected to remain close to a until $w = r_c$ and then with increasing driving force approach zero. Thus the critical nucleus begins to look more and more like a uniformly advancing interface.

4. THE SCREW MECHANISM IN A DIFFUSE INTERFACE

When a dislocation having a Burgers vector with a component normal to the surface intersects the surface, it gives rise to a step which must always terminate at the intersection.[1] When a driving force is applied which favours one phase over the other this step will move and because it is anchored will rotate about the dislocation. The part of the step at large distances from the dislocation will have a much greater distance to travel per revolution and so will lag behind causing the step to form a spiral. A steady state spiral will be reached after a while where the retarding forces due to the curvature of the edge and geometrical factors combine to give each part of the spiral equal angular velocity. With increasing driving force the spiral rotates more rapidly and the spiral arms are closer together. The growth velocity is given by[1]

$$G = \frac{\omega a}{2\pi}$$

and ω the angular velocity of spiral is given approximately by

$$\omega = \frac{V_\infty}{2r_c}$$

where V_∞ is the velocity of a straight step for this driving force and r_c is the radius of a two dimensional nucleus also for this driving force. The spacing between arms of the spiral is equal to $2r_c$.

This theory is independent of the assumption about the sharpness of the interface and should hold until the driving force is so large that the spacing between arms is comparable with the width of a step. This again is given by

$$w < r_c = -\frac{\varepsilon}{a\Delta F_v}$$

or

$$-\Delta F_v < \frac{\sigma_0 g_{\max}}{a}.$$

As ΔF_v becomes greater than $(\sigma_0 g_{\max})/a$ the steady state spiral arms begin to overlap giving a more or less continuous slope instead of a spiral ramp. Until the critical driving force is reached, growth must still be considered as occurring by a lateral mechanism for the advance originates at the screw dislocation.

SUMMARY AND DISCUSSION

It has been shown that the mechanism of the motion of an interface in a crystalline material depends on the driving force rather than on the nature of the interface. At sufficiently large driving forces, the interface can move uniformly without the benefit of either a nucleation or screw mechanism. What constitutes a sufficiently large driving force depends on the diffuseness of the interface, so that for very diffuse interfaces any perceptible driving force will be sufficient, whereas for sharp interfaces the necessary driving force is so large that it may be difficult to achieve.

The intuitive feeling that non-singular interfaces should be able to grow without the benefit of steps is not quite justified but in many cases the necessary driving force before this is so will be quite small. It may even be so small that the difference in driving force resulting from a nonequilibrium shape will be sufficient to let the crystal or surface approach the equilibrium shape dictated by the Wolff construction. For such a case it will never be possible to produce a crystal with flat surfaces by growing at a sufficiently low applied driving force since, if the incremental driving force due to the nonequilibrium shape is sufficiently large, it will enable the crystal surfaces to achieve the other orientations. But many non-singular surfaces will not be so extreme so that the driving force necessary to move them uniformly will be appreciable and these must rely on a nucleation or screw dislocation mechanism.

At small driving forces, the lateral growth mechanisms will be found, either the screw dislocation spiral or, in the absence of a screw dislocation, the two dimensional nucleation mechanism. The step energies and step widths for diffuse interfaces were computed. Since these steps tend to be quite wide, allowance must be made in the lateral growth mechanisms when the scale of the important features of these mechanisms becomes of the order of the step width. It was found convenient to distinguish according to the driving force $-\Delta F_v$ as follows.

(1) For $0 < -\Delta F_v < \sigma_0 g_{\max}/a$ classical lateral growth mechanisms should be observed. By this we mean that in this range the growth is governed by phenomena which can be understood in terms of a step energy ε which is independent of ΔF_v and is given by equation (2.4) or (2.5).

(2) For $\sigma_0 g_{\max}/a < -\Delta F_v < \pi\sigma_0 g_{\max}/a$ the lateral growth mechanism has to be modified to take into account that the size of the critical nucleus and the spacing of the spiral arms are comparable with the step width. In this region a gradual transition is made from classical lateral growth to uniform advance of the interface normal to itself.

(3) For $-\Delta F_v > \pi\sigma_0 g_{\max}/a$ the interface can advance normal to itself without the benefit of the lateral motion of steps.

The application of these principles to solidification kinetics will be discussed in a subsequent paper.[12]

ACKNOWLEDGMENTS

I am indebted to C. P. Bean, J. C. Fisher, G. Horvay, R. Kikuchi and D. S. Rodbell for many helpful discussions and to J. E. Hilliard and D. Turnbull for critical reviews. I am especially indebted to G. W. Sears and D. A. Vermilyea for their encouragement and continued interest.

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