Layered growth of a two-component crystal (theory)

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A complete system of equations describing the isothermal layered growth of solid solutions is derived by a phenomenological approach in which a step on an atomically smooth crystal face is treated as a line singularity. The step is described by either one or three kinetic parameters, depending on the diffusive permeability of the interface. The kinetics of a step is similarly described for the layered growth of a single-component crystal from a melt with allowance for heat conduction. A method is proposed for taking into account the adsorption mechanism for layered growth, and its effect is studied in the single-component and two-component cases. The problem of the velocity of an isolated step over an atomically smooth face is solved as an example.

I. INTRODUCTION

The mechanism for the motion of the interface during the growth of a crystal depends strongly on the properties of the interface. Growth on atomically rough surfaces requires only that the barrier for the incorporation of individual atoms be surmounted, and if the deviation from equilibrium is only slight the growth rate is proportional to the supersaturation.

Atomically smooth faces grow through a tangential motion of steps (layered growth). The steps themselves are rough, so that the velocity at which they move is proportional to the supersaturation. For the motion of an atomically smooth interface, however, the steps must be created as well as moved. Steps can arise only when a dislocation emerges at the interface or as a result of two-dimensional nucleation. In either case, the growth rate of the face is a nonlinear function of the supersaturation. The fundamental theory of layered growth in single-component systems is set forth by Burton, Cabrera, and Frank.[1]

At phase equilibrium in a two-component system, the chemical potentials of each component in the crystal and in the melt are equal. Upon a deviation from equilibrium, the differences in chemical potentials drive fluxes of atoms across the interface. In the case of an atomically rough surface, these fluxes are included in the local boundary conditions, which are mass-balance conditions at each point on the interface.[2] These boundary conditions describe the growth rate as a function of the local supersaturation and also the diffusion flux, which is a measure of the exchange of the atoms of the various species across the interface.

Atoms cannot become attached on atomically smooth surface regions free of steps. In contrast with a single-component system, however, there may be a purely diffusive exchange of atoms between the phases in this case. The attachment of atoms to the crystal occurs at a step, which is a singularity from the standpoint of the macroscopic equations in the volume. The formulation of kinetic conditions at the step requires special analysis.

To illustrate the new approach we consider the growth of a pure crystal from solution. This problem has been analyzed by Chernov,[3] who used a model for the structure of the step, assuming it to be a semicylinder of microscopic radius and assigning it a certain kinetic coefficient. We will treat this problem in a phenomenological way, without specifying the particular structure of the step, and we will show that the kinetics of the step is described by a single parameter. By the same approach we will then derive the complete system of equations describing the layered growth of a two-component crystal. We discussed the kinetics of the motion of a single step, and, finally, we discussed the applicability of this method to real systems, including systems in which adsorption is significant.

GROWTH OF A PURE CRYSTAL

We consider a rectilinear step moving at a velocity v over an atomically smooth face of a crystal growing from solution. The concentration field is described in the coordinate system moving with the step by the diffusion equation

$$\frac{\partial c}{\partial t} - v \frac{\partial c}{\partial x} = D \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial z^2} \right). \tag{1}$$

Here c is the relative fraction of the atoms of the precipitated component, and D is the diffusion coefficient. The x axis is the direction along which the step is moving; the z axis is perpendicular to the interface, with the solution occupying the region $z = 0$. Everywhere on the $z = 0$ interface we impose the condition of zero flux, $\partial c/\partial z = 0$, except at the position of the step. From the standpoint of the macroscopic diffusion equation, the step—a linear singularity in a plane—is described by introducing a δ-function source (more precisely, a sink):

$$D \frac{\partial c}{\partial z} \bigg|_{z=0} = \alpha \delta(x). \tag{2}$$

We are omitting the higher-order moments $\delta'(x), \delta''(x)$, etc., which would be present in a singularity of the general source type, and we are also ignoring the finite height of the step, since these factors fade in importance rapidly with distance and therefore reduce to a restriction on the diffusion equation with boundary condition (2) within short distances of the step. A restriction of the same sort arises from the specif-

ic microscopic structure of the step. In particular, at distances less than the distance between the jogs on the step, two-dimensional equation (1) may not be valid.

The distance a^*, which sets a lower limit on the range of applicability of equation (1) with boundary condition (2), may be regarded as a characteristic dimension of the step. We wish to emphasize that this dimension, only the order of magnitude of which is determined physically, does not appear in any of our results. It figures only in certain intermediate expressions, as a parameter used to form dimensionless variables.

Near the step, but at distances greater than a^* from the step, we can ignore both the time variation and the convective term in diffusion equation (1). A solution of this equation with boundary condition (2) can then be written

$$c(x,z) = \frac{\alpha}{\pi D} \ln \frac{r}{a^*} + \frac{A}{\pi}; \qquad r = (x^2 + z^2)^{1/2}. \qquad (3)$$

We measure the concentration from the equilibrium value c_E. At thermodynamic equilibrium we then have $\alpha = 0$ and $A = 0$. When there is a small deviation from equilibrium, we have in linear thermodynamics a linear relationship between the constant A and the source α: $A = W\alpha$, where W is a kinetic coefficient. The concentration distribution in (3) near the step then becomes

$$c(r) = \frac{\alpha}{\pi D} \ln \frac{r}{a}, \qquad a = a^* \exp(-WD). \qquad (4)$$

The source strength α can be expressed on the basis of mass conservation in terms of the step velocity

$$\alpha = vh(1 - c_E)\Omega_L / \Omega_S,$$

where h is the height of the step, and Ω_L and Ω_S are the atomic volumes in the solution and in the crystal, respectively.

The relationship between the step velocity v and the supersaturation of the solution, which is determined by the macroscopic boundary conditions, is found from the condition that expression (4) be the same as the asymptotic solution of the diffusion equation under boundary condition (2) at small values of r. In this case the sole parameter—which completely describes the kinetic properties of the step—is the "kinetic" dimension a.

Instead of treating a step as a singularity in the macroscopic diffusion equation, Chernov[3] used a model of a step: a semicylinder with a radius equal to the actual height of the step. He specified the boundary condition on the semicylinder in the form standard for a rough surface:

$$D\partial c/\partial r = \beta(c - c_E) = v\Omega_L(1 - c_E)/\pi\Omega_S,$$

where β is a kinetic coefficient.

From the standpoint of our phenomenological approach, Chernov's model corresponds to a characteristic step dimension $a^* = h$ and to the parameter values $W = (a^*\beta)^{-1}$ and $a = a^* \exp(-D/\beta a^*)$. Since the parameter

a completely describes the kinetics of the step (the kinetic coefficient β appears only combined with a in all the results of Ref. 3), these two approaches are essentially equivalent. However, our phenomenological approach is preferable in that it is not based on a model.

GROWTH OF A TWO-COMPONENT CRYSTAL

We consider the isothermal growth a two-component crystal consisting of atoms of species A and B. For definiteness, we assume that the crystal is a substitutional solid solution. We denote by c the atomic fraction of component B. The concentration fields in the initial melt, c_L, and in the crystal, c_S, satisfy the diffusion equation

$$\frac{\partial c_{L,S}}{\partial t} - v \frac{\partial c_{L,S}}{\partial x} = D_{L,S} \left(\frac{\partial^2 c_{L,S}}{\partial x^2} + \frac{\partial^2 c_{L,S}}{\partial z^2} \right) \qquad (5)$$

with the diffusion coefficients D_L and D_S. Here and below, the subscripts L and S refer to the melt and to the crystal, respectively.

A diffusive exchange of atoms between phases (without a change in the total number of particles in either phase) can occur across an interface free of steps:

$$\frac{D_L}{\Omega_L} \frac{\partial c_L}{\partial z} = \Gamma[(\mu_B - \mu_A)_L - (\mu_B - \mu_A)_S] = \frac{D_S}{\Omega_S} \frac{\partial c_S}{\partial z}. \qquad (6)$$

Here μ_A and μ_B are the chemical potentials of atoms A and B, respectively, and the kinetic coefficient Γ is a measure of the diffusive penetrability of the interface. At thermodynamic equilibrium, the chemical potentials of the components in the two phases are equal, and there are no fluxes. We denote the corresponding equilibrium concentrations by c_{LE} and c_{SE}, and we measure the instantaneous values of c_L and c_S from these equilibrium concentrations. The chemical potentials are related to the average free energy per atom (f) by

$$\mu_A = f - c \frac{df}{dc}, \qquad \mu_B = f + (1 - c) \frac{df}{dc}.$$

The chemical-potential difference in (6) can then be written for a small deviation from equilibrium in the form

$$(\mu_B - \mu_A)_L - (\mu_B - \mu_A)_S = f_L'' c_L - f_S'' c_S.$$

Here the second derivatives $f''_{L,S}$ are evaluated at the equilibrium values of the concentrations (for stable phases we have $f''_{L,S} > 0$).

For convenience and for greater symmetry in the resulting equations, we introduce the notation

$$\tilde{c}_j \equiv c_j f_j'', \qquad \tilde{D}_j \equiv D_j / \Omega_j f_j'' \quad (j = L, S).$$

From the standpoint of the macroscopic equations, a step is a singularity. By analogy with the single-component case, we describe this singularity by a compact flux across the interface. The boundary condition at $z = 0$ is then

$$\tilde{D}_L \frac{\partial \tilde{c}_L}{\partial z} - \alpha_L \delta(x) = \Gamma(\tilde{c}_L - \tilde{c}_S) = \tilde{D}_S \frac{\partial \tilde{c}_S}{\partial z} - \alpha_S \delta(x). \qquad (7)$$

The strength of this compact flux differs on the two

sides of the interface, in accordance with the ability of the step to move. The relationship between the step velocity v and the sources α_L and α_S is determined by the conservation of the number of particles. The total fluxes of the atoms of species A and B through the step from the melt into the crystal are

$$I_A = -\alpha_L + \Omega_L^{-1}(hv+j)(1-c_{LE}) = -\alpha_S + \Omega_S^{-1}hv(1-c_{SE}), \quad (8a)$$

$$I_B = \alpha_L + \Omega_L^{-1}(hv+j)c_{LE} = \alpha_S + \Omega_S^{-1}hvc_{SE}, \quad (8b)$$

where h is the height of the step, and j is the convective flux through the step. This flux arises in the melt because of the difference between the atomic volumes Ω_L and Ω_S; as follows from (8), this flux is

$$j = hv(\Omega_L - \Omega_S)/\Omega_S.$$

For the velocity v we find from (8)

$$v = \Omega_S(\alpha_S - \alpha_L)/h(c_{LE} - c_{SE}). \quad (9)$$

Condition (7), along with the macroscopic boundary conditions, unambiguously determines the solution of diffusion equations (5). A lower limit is set on the range of applicability of this solution by the characteristic dimension of the step a^*; everything we said in the preceding section for the single-component case also applies to this dimension.

To proceed further toward the derivation of phenomenological equations for the sources α_L and α_S, we require that any possible effect of a time variation and of convection [the left side of Eqs. (5)]—which in principle falls off toward the singularity—become negligibly small quite close to the step, even at distances greater than a^* from the step. In other words, near the step there must be a region of dimension $l \gg a^*$ in which the concentration distribution is described by the solution of a Laplace equation with boundary condition (7), specifically,

$$\tilde{c}_{L,s} \approx \frac{\alpha_L - \alpha_s}{\pi(\tilde{D}_L + \tilde{D}_s)} \ln \frac{r}{a^*} \pm \tilde{D}_{L,s}^{-1} \frac{\tilde{D}_s \alpha_L + \tilde{D}_L \alpha_s}{\pi(\tilde{D}_s + \tilde{D}_L)} \cdot$$
$$\cdot \mathrm{Re}\left\{\frac{\mathrm{Ei}[-a_0^{-1}(z-ix)]}{\exp[-a_0^{-1}(z-ix)]}\right\} + c_{L,s}^0,$$
$$a_0^{-1} \equiv \Gamma(\tilde{D}_L^{-1} + \tilde{D}_s^{-1}). \quad (10)$$

Here $\mathrm{Ei}(\xi)$ is the integral exponential function. Here and below, the upper sign in (10) refers to $\tilde{c}_L$, and the lower sign to $\tilde{c}_S$. The constants c represent the leading term (which does not decay toward the step) of the general solution of the diffusion equations without sources.

The dimension a_0 introduced in (10) is a measure of the effect of the diffusive permeability of the boundary. The discussion below and the form of the phenomenological equations depend on the relation between a_0 and the step size a^*.

1. *Boundary of low permeability.* At $a^* \ll a_0$ the permeability of the boundary near a step is inconsequential, and the concentration distribution at $a^* \ll r \ll a_0$, found from (10), can be written in the form

$$\tilde{c}_{L,s} = \pm \frac{\alpha_{L,s}}{\pi \tilde{D}_{L,s}} \ln \frac{r}{a^*} \pm \frac{A_{L,s}}{\pi}.$$

A complete equilibrium in the system corresponds to $\alpha_L, \alpha_S, A_L, A_S = 0$. Upon a small deviation from equilibrium, the constants $A_{L,S}$ must be related in a linear way to $\alpha_{L,S}$ by means of some symmetric, positive-definite kinetic matrix:

$$A_L = W_L \alpha_L + W \alpha_s, \quad A_s = W \alpha_L + W_s \alpha_s.$$

That the matrix $\widehat{W}$ is symmetric can be easily seen by writing, for example, an expression for the entropy production in a small cylindrical region around the step. Introducing the "kinetic" dimensions

$$a_{L,s} = a^* \exp(-W_{L,s}\tilde{D}_{L,s})$$

by analogy with the single-component case, and using these dimensions to replace the diagonal elements of the matrix $W_{L,S}$, we find the following expressions for the concentration distribution near the step:

$$\tilde{c}_L = \frac{\alpha_L}{\pi\tilde{D}_L} \ln \frac{r}{a_L} + \frac{W}{\pi}\alpha_s + \frac{\sigma\Omega_s K}{h(c_{SE} - c_{LE})}, \quad (11)$$

$$\tilde{c}_s = -\frac{\alpha_s}{\pi\tilde{D}_s} \ln \frac{r}{a_s} - \frac{W}{\pi}\alpha_L + \frac{\sigma\Omega_s K}{h(c_{SE} - c_{LE})}.$$

These expressions no longer contain the microscopic size of the step. the last terms on the right side of (11) reflect the correction to the concentration for the step curvature k (the Gibbs-Thomson effect), and σ is the linear tension of the step. In this case the kinetics of the step is thus described completely by the three phenomenological parameters a_L, a_S, and W. Expressions (11) completely close the problem. The procedure for solving specific problems can be outlined as follows: Condition (7) at the interface, along with expression (9) for the velocity, can be used to solve macroscopic equations (5) (with specific external boundary conditions) given the values of α_L and α_S. The sources α_L and α_S are then determined unambiguously by the requirement that the asymptotic form of the resulting solution agree with (11) in the limit as $r \to 0$.

Conditions (11) are analogous to the kinetic boundary conditions at an atomically rough surface, which relate the values of the concentration at the interface to the atomic fluxes. The only difference is that the value of the concentration is finite at the interface, while at a step it diverges logarithmically. In the latter case the correct approach is thus to require that the asymptotic form of the solution of the macroscopic equations agree with (11).

2. *Boundary of high permeability.* At $a^* \gtrsim a_0$, the penetrability of the interface is important throughout the macroscopic region. The second term in (10) is of the form z/r^2, analogous to the potential of a two-dimensional electric dipole, and it falls off with distance in proportion to r^{-1}. The discontinuity $c_L^0 - c_S^0$ is the concentrations at the interface, is also negligibly small in this case, so that the concentration distribution near the step can be described by

$$\tilde{c}_{L,s} = \frac{\alpha}{\pi(\tilde{D}_L + \tilde{D}_s)} \ln \frac{r}{a^*} + \frac{A}{\pi},$$

where $\alpha = \alpha_L - \alpha_S$. As in the single-component case, the

linear relationship between A and α upon a small deviation from equilibrium gives us one kinetic parameter a with the dimensionality of a length; as a result we have

$$\tilde{c}_{L,s} = \frac{\alpha}{\pi(\bar{D}_L + \bar{D}_s)} \ln \frac{r}{a} + \frac{\sigma\Omega_s K}{h(c_{SE} - c_{LE})}, \quad (12)$$

where we have added a term for the curvature of the step, as in (11).

In the solution of specific problems in this case there would be no point in introducing arbitrary sources α_L and α_S. The boundary conditions at the interface, which replace (7), and the expression for the step velocity must be written in the form

$$\tilde{c}_L(x,0) = \tilde{c}_s(x,0), \quad \bar{D}_L \frac{\partial\tilde{c}_L}{\partial z} - \bar{D}_s \frac{\partial\tilde{c}_s}{\partial z} = \alpha\delta(x), \quad (13)$$

$$v = \alpha\Omega_s/h(c_{SE} - c_{LE}). \quad (14)$$

We then determine α from the condition that the asymptotic form of the solution of Eq. (5) in the limit $r \to 0$ agree with expression (12). We call this version of the description of the step "single-parameter kinetics," in contrast with the "three-parameter kinetics" obtained in the case $a^* \ll a_0$.

We have thus found that, depending on the diffusive permeability of the interface, Γ, the kinetics of a step at the surface of a two-component crystal can be described by either one or (if Γ is not too large) three parameters. What appears at first glance to be the fundamental distinction between these two cases turns out to be a relative distinction in the sense that any step can be described by single-parameter kinetics in a certain region of external macroscopic conditions. This conclusion follows from the observation that the second of the approaches described here is also completely applicable to the case $a^* \ll a_0$, provided only that the dimension l be greater than a_0 in the region in which we can ignore convective transport, the time variation of the diffusion equation, and the inhomogeneity of the external boundary conditions. In this case we can ignore the second term in (10) at distances r and thereby find a logarithmic distribution (12) with a single "kinetic" parameter a. If $a^* \ll a_0$, i.e., if the step is "actually" described by three parameters, then an expression for a in terms of these parameters can be found by comparing (10) with (12) at $r \gg a_0$ and with (11) at $r \ll a_0$:

$$a = \gamma^{-1} a_0$$

$$\exp\left\{ \frac{(\bar{D}_L^{-1} + \bar{D}_s^{-1})[\ln(a_L\gamma/a_0)\ln(a_s\gamma/a_0) - W_2\bar{D}_L\bar{D}_s]}{\bar{D}_L^{-1}\ln(a_L\gamma/a_0) + \bar{D}_s^{-1}\ln(a_s\gamma/a_0) - 2W} \right\}, \quad (15)$$

where γ is the Euler constant. The three-parameter kinetics of the step thus reduces to single-parameter kinetics, but only as long as the distance over which it is legitimate to replace diffusion equation (5) by a Laplace equation satisfies $l \gg a_0$. If this condition does not hold, the step cannot be described by a single kinetic parameter, so that the step velocity v will depend on a_L, a_S, and W in a way other than in the combination in (15). As the macroscopic dimension l de-

creases to the step size a^* (as a result of an increase in the velocity v, for example), a phenomenological description of the step by means of linear kinetic relations becomes impossible.

An analogous description of the kinetics of a step holds for the case of the growth of a pure crystal from a melt with heat conduction. If there is a limitation on the rate at which heat can be transferred across the interface, a temperature dicontinuity will arise at the interface (the Kapitza discontinuity). In this case the step kinetics is described by three parameters. If the macroscopic dimensions are much larger than the characteristic dimension analogous to a_0, the Kapitza discontinuity becomes inconsequential, and the step can be characterized by a single kinetic parameter.

KINETICS OF AN ISOLATED STEP

To illustrate the use of this approach we consider the motion of an isolated rectilinear step upon a small deviation from equilibrium. There are no fluxes either in the melt or in the crystal far from the step. The concentration in the melt differs from its equilibrium value by an amount c_∞, while that in the crystal differs in accordance with boundary condition (7) from its equilibrium value by an amount $c_\infty f''_L/f''_S$.

The solution of steady-state equations (5) with boundary condition (7) is

$$\tilde{c}_L(x,z) = \int_{-\infty}^{\infty} A_L(k)\exp[ikx - \varkappa_L(k)z]\frac{dk}{2\pi} + c_\infty f_L'', \quad z > 0,$$

$$\tilde{c}_s(x,z) = \int_{-\infty}^{\infty} A_s(k)\exp[ikx + \varkappa_s(k)z]\frac{dk}{2\pi} + c_\infty f_L'', \quad z < 0. \quad (16)$$

Here

$$A_L(k) = \frac{\Gamma(\alpha_s - \alpha_L) - \bar{D}_s\varkappa_s\alpha_L}{\bar{D}_L\bar{D}_s\varkappa_L\varkappa_s + \Gamma(\bar{D}_L\varkappa_L + \bar{D}_s\varkappa_s)},$$

$$A_s(k) = \frac{\Gamma(\alpha_L - \alpha_s) + \bar{D}_L\varkappa_L\alpha_s}{\bar{D}_L\bar{D}_s\varkappa_L\varkappa_s + \Gamma(\bar{D}_L\varkappa_L + \bar{D}_s\varkappa_s)}, \quad (17)$$

$$\varkappa_{L,s}(k) = (k^2 - ikv/D_{L,s})^{1/2}.$$

The sign of the square root is chosen to satisfy the condition $\varkappa_{L,S} \sim |k|$ in the limits $k \to \pm\infty$. We are interested in the asymptotic behavior of expressions (16) at small distances from the step. This asymptotic behavior cannot be found by using the general expressions for A_L and A_S in (17). We first consider the limiting case of low velocities,

$$l = \min\{D_L, D_s\}/v \gg a_0. \quad (18)$$

To evaluate the asymptotic behavior at $a_0 \ll r \ll l$ (we are accordingly using the single-parameter description of the step kinetics), we can replace expression (17) by

$$A_{L,s} = \frac{\alpha_s - \alpha_L}{\bar{D}_L\varkappa_L + \bar{D}_s\varkappa_s}. \quad (19)$$

Substituting (19) into (16), we find $\tilde{c}_{L,S}(x,z)$ at small distances

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from the step (but at distances greater than a_0):

$$\tilde{c}_{L,s}(r) = \frac{\alpha_s - \alpha_L}{\pi(\tilde{D}_L{}^2 - \tilde{D}_s{}^2)}\left[-\tilde{D}_L \ln\left(\frac{vr\gamma}{4D_L}\right) + \tilde{D}_s \ln\left(\frac{vr\gamma}{4D_s}\right)\right.$$

$$-2\tilde{D}_L\tilde{D}_s \left(\frac{D_L - D_s}{D_s\tilde{D}_L{}^2 - D_L\tilde{D}_s{}^2}\right)^{1/2}$$

$$\left.\text{Arctg}\left\{\frac{[(D_L - D_s)(D_s\tilde{D}_L{}^2 - D_L\tilde{D}_s{}^2)]^{1/2}}{D_L\tilde{D}_s + D_s\tilde{D}_L}\right\}\right] + c_\infty f_L''; \tag{20}$$

Here $r = (x^2 + z^2)^{1/2}$, and γ is the Euler constant.

From the condition that the asymptotic behaviors of (20) and (12) agree, using relation (14), we find the following equation for the step velocity:

$$v \ln(va\gamma/4D^*) = \pi(\tilde{D}_L + \tilde{D}_s)f_L''c_\infty/h(c_{LE} - c_{SE}),$$

$$D^* = (D_L D_s)^{1/2}\exp\left\{\frac{1}{2(\tilde{D}_L - \tilde{D}_s)}\left[(\tilde{D}_L + \tilde{D}_s)\ln\left(\frac{D_L}{D_s}\right)\right.\right.$$

$$-4\tilde{D}_L\tilde{D}_s\left(\frac{\tilde{D}_L - \tilde{D}_s}{D_s\tilde{D}_L{}^2 - D_L\tilde{D}_s{}^2}\right)^{1/2}$$

$$\left.\left.\times \text{Arctg}\left\{\frac{[(D_L - D_s)(D_s\tilde{D}_L{}^2 - D_L\tilde{D}_s{}^2)]^{1/2}}{D_L\tilde{D}_s + D_s\tilde{D}_L}\right\}\right]\right\}. \tag{21}$$

If we had found the asymptotic behavior of the solution at $r \ll a_0$, and if we had used (11), we would have found expression (21) again, but with a given by (15). As the velocity increases, condition (18) may be violated. In this case, the simplified expressions in (19) are no longer valid. At sufficiently small Γ we can have a different limiting case:

$$v \gg \Gamma(D_L{}^{1/2}/\tilde{D}_L + D_s{}^{1/2}/D_s)\max\{D_L{}^{1/2}, D_s{}^{1/2}\},$$

in which we can ignore in (17) the terms with Γ. We then find the following expression for $\tilde{c}_{L,S}(r)$ at short distances from the step:

$$\tilde{c}_{L,s}(r) = \pm\frac{\alpha_{L,s}}{\pi D_{L,s}}\ln\left(\frac{vr\gamma}{4D_{L,s}}\right) + c_\infty f_L''. \tag{22}$$

From the condition that (22) agree with (11), we find the following equation for the step velocity:

$$v\left[\ln\left(\frac{va_L\gamma}{4D_L}\right)\ln\left(\frac{va_s\gamma}{4D_s}\right) - W^2\tilde{D}_L\tilde{D}_s\right] \tag{23}$$

$$= \frac{\pi c_\infty f_L''\Omega_s}{h(c_{LE} - c_{SE})}\left[\tilde{D}_L\ln\left(\frac{va_s\gamma}{4D_s}\right) + \tilde{D}_s\ln\left(\frac{va_L\gamma}{4D_L}\right)\right.$$

$$\left. -2W\tilde{D}_L\tilde{D}_s\right].$$

In the cases which arise in practice, we would usually have $D_S/D_L \ll 1$, $W\tilde{D}_L \lesssim 1$. Expressions (21) and (23) for the velocity v would then become the same,

$$v \ln\left(\frac{va_L\gamma}{4D_L}\right) = \pi\frac{\Omega_s D_L c_\infty}{\Omega_L h(c_{LE} - c_{SE})}, \tag{24}$$

from which we find, with logarithmic accuracy,

$$v = \pi\frac{\Omega_s D_L c_\infty}{\Omega_L h(c_{LE} - c_{SE})}\left[\ln\left(\frac{\pi\Omega_s a_L\gamma c_\infty}{\Omega_L h(c_{SE} - c_{LE})}\right)\right]^{-1}. \tag{25}$$

The step velocity v in (25) is a nonlinear function of the supersaturation c_∞. The reason is that the characteristic distance D_L/v over which the logarithmic distribution is violated and the concentration approaches the value c_∞ depends on the velocity v. Purely diffusive mass transfer is generally produced not throughout the melt but only in a diffusion boundary layer of dimension δ. If this dimension is smaller than D_L/v (as is always true in the limit of an extremely low supersaturation), this dimension δ will appear in place of D_L/v in the logarithm in (24), and the velocity v will be a linear function of the supersaturation.

We could discuss other problems of interest in the theory of the layered growth of crystals by an analogous approach. In particular, a study of two-dimensional nucleation at an atomically smooth face requires consideration of an annular step and the incorporation of a term proportional to the step curvature in the boundary asymptotic expression (12). For an analysis of the motion of steps in echelon (the growth of a vicinal face), one would have to require that the concentration distribution near each step agree with (12).

DISCUSSION OF APPROXIMATIONS

We have examined the isothermal crystallization of a solid solution under the assumption that the state of the crystal and of the melt can be characterized completely by specifying the fields of the relative component concentrations $c_S(r)$ and $c_L(r)$. This assumption means that, first, at a given temperature there are no effects of stratification or ordering in the crystal; i.e., the mixing energy is quite small. Second, the concentration of vacancies and of interstitials is assumed to be negligibly small, as a result of the high formation energy of these defects. Third, we are ignoring secondary effects of the onset of stresses in the crystal accompanying the nonuniform distribution $c_S(r)$ and the convection fluxes upon a redistribution of the $c_L(r)$. In this situation, which is typical during the growth of solid solutions, the relaxation of each of the fields $c_s(r)$ and $c_L(r)$ is described completely by a single diffusion coefficient (D_S or D_L), whose magnitude is determined by the specific microscopic mechanism.

A more important approximation is to ignore adsorption at the interface between the crystal and the liquid. In all the derivations above it was assumed that the crystal grows as a result of the supply of atoms directly from the volume of the liquid to the step. We have ignored the alternative growth mechanism in which atoms from the melt initially enter an adsorbed layer on the surface and later cross the step and enter the crystal. These two mechanisms for the entry of atoms into the crystal work in parallel and should, in general, be considered jointly.[1] To do so will not complicate the phenomenological description in a fundamental way, since the adsorbed layer is an ordinary boundary for the interior, as the step is for the adsorbed layer; it does not constitute a singularity as a step does for the bulk diffusion equa-

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tion. All the additional coefficients can be introduced in the standard way. However, because of the increase in the number of parameters and variables, the general equations become unacceptably complicated, and the number of different limiting cases increases catastrophically.[1]

We will therefore be content with a more restricted analysis of the growth of a pure crystal from a solution; from this analysis we can draw qualitative conclusions about the effect of adsorption in more general cases. Furthermore, it is in this restricted case that the adsorption seems to be most important. Introducing an adsorbed layer with a relative concentration $c_A(x)$ and a diffusion coefficient D_A, which exchanges atoms with the solution at a characteristic rate τ^{-1}, we replace Eqs. (1) and (2) by the system

$$\frac{\partial c}{\partial t} - v\frac{\partial c}{\partial x} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial z^2}\right), \tag{26a}$$

$$D\frac{\partial c}{\partial z}\bigg|_{z=0} = \alpha\delta(x) - \varkappa\tau^{-1}[c_A(x) - pc(x,0)], \tag{26b}$$

$$\frac{\partial c_A}{\partial t} - v\frac{\partial c_A}{\partial x}$$

$$= D_A\frac{\partial^2 c_A}{\partial x^2} - \tau^{-1}[c_A(x) - pc(x,0)] - Bc_A(0)\delta(x). \tag{26c}$$

Here $\varkappa$ is the ratio of the atomic area in the adsorbed layer to the atomic volume in the solution (Ω_L), the dimensionless parameter p is a measure of the adsorption rate, and the kinetic coefficient B describes the exchange of atoms between the step and the adsorbed layer. As usual, c_A and c are reckoned from their equilibrium values. The step velocity v is related to the sources in Eqs. (26b) and (26c) by mass conservation:

$$\alpha + B\varkappa c_A(0) = vh(1-c_E)\Omega_L/\Omega_S.$$

The general solution of system (26) in region $r\ll l$, where the time variation and convection can be ignored in the diffusion equations, is

$$\pi Dc(x,z)$$
$$= (\alpha+\alpha_A)\ln(r/a) + l_p\int_0^\infty \frac{\alpha+\alpha_A+\alpha_A l_\tau k}{1+l_p k+l_p l_\tau k^2}e^{-kz}\cos(kx)\,dk,$$

$$\pi Dc_A(x)/p =$$
$$(\alpha+\alpha_A)\ln(r/a) + l_p\int_0^\infty \frac{\alpha+\alpha_A(1-l_\tau/l_p)+(\alpha+\alpha_A)k}{1+l_\tau k+l_p l_\tau k^2}\cos(kx)\,dk,$$
$$\tag{27}$$

$$l_p = D_A\varkappa p/D, \quad l_\tau = D\tau/\varkappa p,$$

where a is some constant dimension, and the strengths of the sinks from the volume (α) and from the adsorbed layer (α_A) are related by an equation which follows from

$$\alpha_A = B\varkappa c_A(0).$$

From (27) we see that at large distances, $r\gg\max\{l_p, (l_p l_\tau)^{1/2}\}$ we have

$$c(x,z) = \frac{\alpha+\alpha_A}{\pi D}\ln\frac{r}{a}, \quad c_A(x) = \frac{c(x,0)}{p}; \tag{28}$$

i.e., in this region the diffusive flux goes through the volume. This result means that under the condition

$$l\gg\max\{l_p, (l_p l_\tau)^{1/2}\} \tag{29}$$

it is sufficient to consider only the volume diffusion equation and to describe the kinetic properties of the step by the single phenomenological parameter a, as in the situation discussed at the beginning of this paper. However, the processes associated with the presence of the adsorbed layer generally affect the dimension a. In particular, an upper limit is imposed on a by the condition that expressions (27) retain their sign over the entire macroscopic region $r\gg a^*$.

If inequality (29) does not hold, the asymptotic behavior in (28) cannot be attained, and the kinetics of the step must in general be described by two parameters. To illustrate this situation we consider the particular case in which both of the lengths l_τ and $(l_p l_\tau)^{1/2}$ are macroscopic:

$$\min\{l_\tau, (l_p l_\tau)^{1/2}\}\gg a^*. \tag{30}$$

We thus see from (27) that the concentration distributions near the step, i.e., at $a^*\ll r\ll\min\{l_\tau, (l_p l_\tau)^{1/2}\}$, are of the form

$$c_A(x) = \frac{\alpha_A}{\varkappa B}\left(1 + \frac{|x|B}{2D_A}\right), \quad c(x,z) = \alpha\ln(r/a_1),$$

which means that there is a complete separation of volume diffusion from surface diffusion. The constant dimension a_1 is a second (after B) phenomenological parameter, which describes the kinetics of the step with respect to the volume, and system (26) must be supplemented with the requirement that the asymptotic form of $c(x,z)$ as $r\to 0$ coincide with $\alpha\ln(r/a_1)$.

Under inequality (30), the "microscopic" kinetic dimension a, corresponding to the single-parameter situation, (29), can be expressed in terms of the two microscopic parameters a_1 and B as follows:

$$\ln\frac{a}{a_1}$$
$$= \frac{\ln^2(\gamma(l_p l_\tau)^{1/2}/a_1) + \pi D(1-4l_\tau/l_p)^{-1/2}\xi/B\varkappa p - \xi^2/4}{\ln(\gamma(l_p l_\tau)^{1/2}/a_1) + \pi D/B\varkappa p - (1/2 - l_\tau/l_p)(1-4l_\tau/l_p)^{-1/2}\xi}.$$
$$\xi = \ln[(1+(1-4l_\tau/l_p)^{1/2})/(1-(1-4l_\tau/l_p)^{1/2})]. \tag{31}$$

Under condition (30), the right side of this expression is positive, in accordance with the circumstance that the adsorption mechanism can only increase the effective permeability of the step, so that we have $a\geq a_1$. In the limit $a_1\to 0$, in which atoms cannot enter the crystal directly from the volume, a_1 generally drops out of (31), and the dimension a becomes determined exclusively by the adsorption mechanism.

In the case of strong adsorption $(p\gg 1)$, with the natural order of magnitude of the quantities $D\sim D_A\sim B\varkappa$, $a_1\sim\varkappa$, $l_p/l_\tau\gg 1$ we find $a=\gamma l_p$ from (31). This result means that in the case of strong adsorption the parameter a is relatively

insensitive to the microscopic structure of the step and is determined exclusively by the macroscopic length l_p.

When adsorption is weak ($p \sim 1$), the characteristic lengths l_p and l_r are generally of microscopic size. In this case we cannot resolve the flux to the step into two-dimensional and three-dimensional components, and the kinetics of the step is described by the single phenomenological parameter a.

In contrast with the growth of a pure crystal from solution, in the case of the crystallization of a two-component crystal from a melt there are no special reasons for a strong adsorption. In this sense, the theory derived here for the growth of a two-component crystal with allowance for adsorption effects may have a rather broad range of applicability.

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[1)]The situation is aggravated by the circumstance that in the two-component case it is generally necessary to introduce two adsorbed layers, one on each side of the surface, and to consider the exchange of atoms between each of these layers and the crystal and the melt.

[1]W. Burton, N. Cabrera, and F. Frank, Philos. Trans. R. Soc. London **A243**, 299 (1951).
[2]D. E. Temkin, Fiz. Met. Metalloved. **24**, 207 (1967).
[3]A. A. Chernov, Usp. Fiz. Nauk **73**, 277 (1961) [Sov. Phys. Usp. **4**, 116 (1961)].

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