AN ANALYSIS OF COMBINED SURFACE AND VOLUME DIFFUSION PROCESSES IN CRYSTAL GROWTH

II. ASYMMETRIC CAPTURE AT STEPS

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We consider the terrace-ledge-kink model of crystal growth, and formulate coupled volume and surface diffusion equations. These govern the flow of growth units from a supersaturated fluid phase, through a stagnant layer, and across terraces to a series of parallel steps on a crystal surface. We obtain a steady state solution and the growth rate of vicinal surfaces with equidistant steps when each step can exchange growth units with its two adjacent terraces at unequal rates (asymmetric capture). Diffusion to an isolated step is considered in detail since the resulting surface current determines the general form of the growth rate vs supersaturation curve, and gives precise information on the parabolic region of this curve. Three regimes of diffusion are observed depending on the relative surface and volume diffusion rates, and on the rate of exchange between the fluid and the surface. For an isolated step, small surface diffusion rates and slow exchange define a regime where volume density gradients are negligible, and the classical Burton, Cabrera, and Frank expression for the surface diffusion current is valid. Intermediate surface diffusion and exchange rates cause significant volume density gradients, and nearly cylindrical density contours surrounding a step. Very large surface diffusion and exchange rates cause large portions of the surface to act as a catchment area for a step and the volume density contours assume a nearly planar geometry. Asymmetric capture kinetics at a step influence the geometry of the diffusion field only in the latter case of very large surface diffusion rates. For an array of parallel and equidistant steps, the parabolic region of the growth rate versus supersaturation curve is sensitive to the various diffusion and exchange processes. It measures the distance at which neighboring steps can interact. Changes in the shape and extent of this region with the thickness of the stagnant layer (or the rate of stirring) allow an experimental determination of the model parameters.

1. Introduction

The terrace-ledge-kink (TLK) model of crystal surfaces provides a convenient framework for describing surface structures and for calculating growth rates of surfaces near close-packed orientations. Growth units move through a supersaturated fluid to the crystal surface and then along the surface until they reach kink sites in steps. The resulting lateral motion of steps has been detected by Bethge's gold decoration technique. Bennema et al. have recently reviewed the experimental evidence for crystal growth kinetics according to this model.

The general volume-surface-edge transport problem includes the following processes: (a) diffusion of growth units through the supersaturated fluid to the crystal surface, (b) adsorption-desorption on the terraces between steps, (c) surface diffusion along the terraces to the steps, (d) capture at the step edges, (e) edge diffusion to kink sites, and (f) capture at kink sites. Because of their mathematical complexity, the resulting transport equations have not been solved. Indeed, most calculations avoid coupled volume and surface diffusion by assuming either that processes (b), (c) and (d) are rate limiting for vapor growth, or that processes (a) and (d) are rate limiting for solution growth [2,6,7] (processes (b) and (c) are then excluded]. We note that coupled diffusion equations have been presented by Birman and Timan (although no solution was given for isothermal mass transport), and that such equations have been considered in electrocrystallization phenomena.

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In a previous paper\textsuperscript{10}, hereafter referred to as I, we solved the coupled surface and volume diffusion equations resulting from processes (a)-(d) under steady state conditions. The steps were treated as uniform line sinks, assuming a high kink density and a large edge diffusion coefficient. However, widely spaced kinks or slow edge diffusion can cause a dramatic reduction of the growth rate\textsuperscript{2,11}. The method of solution in I was predicated on the assumption of symmetric capture at the steps, i.e., adsorbed growth units have the same attachment and detachment rates, regardless of the direction from which they approach the step. Experimental evidence\textsuperscript{12,13} indicates that steps often present an asymmetric barrier for molecular exchange, and thus invalidates our basic assumption in I. Furthermore, Schwoebel et al.\textsuperscript{14,15} have shown that asymmetric capture conditions at steps may cause a step train to become unstable and to form bunches. These can be the origin of macrosteps and of other macroscopic morphological features.

This paper extends I to the case of asymmetric step capture. Some of the following results have been presented elsewhere\textsuperscript{10}). We retain the other basic assumptions in I: slow straight equidistant steps, steady state conditions, and steps considered as line sinks. These will be relaxed in future work. Section 2 presents the transport equations for the TLK model, and in section 3 we obtain an analytical solution in the form of a Fourier series. In sections 4 and 5 we present numerical results, and a detailed description of the surface and volume diffusion fields as a function of the relevant physical parameters. Section 4 pertains to the diffusion processes for an isolated step; section 5 deals with the growth rate that results from the model for equidistant steps.

2. Coupled surface and volume diffusion equations

Consider a sequence of parallel equidistant steps on a crystal surface as represented in fig. 1. The y-direction is taken normal to the close-packed terraces, and the step spacing is \( l \). As shown in I, the volume and surface densities of growth units, \( N(x,y) \) and \( n(x) \), must obey the coupled system of equations.

\[
\frac{\partial^2 N}{\partial x^2} + \frac{\partial^2 N}{\partial y^2} = 0, \quad 0 < x < l, \quad 0 < y < \delta. \tag{2.1}
\]

\[
D_s \frac{d^2 n}{dx^2} + D \frac{\partial N}{\partial y} \bigg|_{y=0} = 0, \quad 0 < x < l, \tag{2.2}
\]

\[
D \frac{\partial N}{\partial y} \bigg|_{y=0} = \frac{D}{A} N \bigg|_{y=0} - \frac{n}{\tau}, \quad 0 < x < l, \tag{2.3}
\]

where \( D \) and \( D_s \) are the volume and surface diffusion coefficients, \( D/A \) is the rate of adsorption, and \( \tau \) is the lifetime of an adsorbed growth unit on the terraces. The parameter \( A \) describes the kinetics of entering the adsorbed layer. If this process does not require an activation energy larger than that required for volume diffusion, \( A \) is approximately the mean free path in the fluid phase. Eq. (2.1) is the usual steady state diffusion equation; eq. (2.2) states that surface diffusion is fed by a volume flux, and eq. (2.3) expresses this flux in terms of an assumed first order adsorption-desorption reaction, \( D/A \) and \( \tau^{-1} \) being the forward and reverse reaction constants. Growth units are supplied from the top of an unstirred layer of thickness \( \delta \) where a fixed supersaturation \( \sigma \) prevails:

\[
N(x,\delta) = N_0 (1 + \sigma). \tag{2.4}
\]
The equilibrium values $N_0$ and $n_0$ of $N(x,y)$ and $n(x)$ are related according to

$$n_0/\tau = D N_0 / \lambda,$$

(2.5)

because, at equilibrium, the flux (2.3) must vanish identically. Finally we assume that, at steady state, the magnitude of the surface currents to the right and left of a step furnish growth units which are captured according to first order kinetics. Therefore we have the boundary conditions:

$$j_0 \equiv D_s \frac{dn}{dx} \bigg|_{x=0^+} = k_o [n(0^+)-n_0],\quad (2.6)$$

$$j_1 \equiv -D_s \frac{dn}{dx} \bigg|_{x=0^-} = k_l [n(0^-)-n_0].\quad (2.7)$$

The surface currents $j_0$ and $j_1$ are clearly positive for growth (negative for dissolution), and $j_0 + j_1$ is the total current to the step at $x = 0$. The asymmetry of the steps is built into the inequality of the capture rates $k_0$ and $k_l$; the solution given in I results when $k_0 = k_l$. Because of the periodicity in the $x$-direction, eq. (2.7) can also be written as

$$j_1 \equiv -D_s \frac{dn}{dx} \bigg|_{x=1^-} = k_l [n(1^-)-n_0].\quad (2.8)$$

Unequal values of $k_0$ and $k_l$ imply that the volume and surface densities have no symmetry plane, i.e., their distribution is skewed. Thus $\partial N/\partial x \neq 0$ at step positions, and $n(x)$ is discontinuous at these points. The mathematical analysis is therefore expected to be considerably more complex than in I.

Before proceeding to the analytical solution of the systems of equations (2.1)–(2.8), we introduce the following convenient dimensionless variables

$$x \rightarrow x / \lambda, \quad y \rightarrow y / \delta, \quad l \rightarrow l / \lambda, \quad \delta \rightarrow \delta / \lambda,$$

(2.9)

where, according to the Einstein relation,

$$\lambda = (D_s \tau)^{1/2},$$

(2.10)

is the well known mean surface diffusion distance. In terms of the new unknown functions

$$u(x,y) = D \tau N(x,y), \quad s(x) = \lambda n(x)$$

(2.11)

and currents

$$q_0 \equiv \frac{ds}{dx} \bigg|_{x=0^+} = \frac{\lambda A}{D_s} j_0, \quad q_1 \equiv -\frac{ds}{dx} \bigg|_{x=0^-} = \frac{\lambda A}{D_s} j_1,$$

(2.12)

Eqs. (2.1)–(2.8) assume the form

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} = 0, \quad 0 < x < l, \quad 0 < y < \delta,$$

(2.13)

$$\frac{d^2 s}{dx^2} - s + u(x,0) = 0, \quad 0 < x < l,$$

(2.14)

$$1 \frac{\partial u}{\partial y} (x,0) = u(x,0) - s, \quad 0 < x < l,$$

(2.15)

$$u(x,\delta) = u_0 (1 + \sigma),$$

(2.16)
The dimensionless ratios of kinetic coefficients (2.20) control the relative importance of the various diffusion and adsorption-desorption processes. The parameters $h_0$ and $h_1$ (unequal a priori) describe the relative impedance due to surface diffusion and to capture at steps. For example, small values of $h_0$ and $h_1$ indicate that the mean surface diffusion velocity $D_{ij} \dot{j} = \dot{j}/\tau$ [cf. eq. (2.10)] is much slower than the rates of capture $k_0$ and $k_1$; the surface density adjacent to the steps is then anchored near its equilibrium value as is readily seen with eqs. (2.18)-(2.19). The “coupling parameter” $h$ controls the magnitude of the volume gradients which result from surface processes. For example, we showed in [1] that, for $A \to \infty$, $D \to \infty$, but $D/A$ finite (which implies $h \to 0$), the Burton-Cabrera-Frank (BCF) theory is valid and that volume gradients are negligible. In their theory a constant density $N_0(1+\sigma)$ is assumed throughout the volume. On the other hand, for $h \gg 1$, surface processes can induce strong volume gradients. In accordance with eq. (2.15), the volume density adjacent to the surface is then approximately proportional to the surface density, i.e., these densities are strongly coupled and we expect long range effects owing to volume gradients which are then set up.

3. Solution of the diffusion equations

We introduce the following formal Fourier expansions for equidistant steps

$$u_0 = s_0, \quad (2.17)$$

$$h_0 q_0 = s(0+), \quad s_0, \quad (2.18)$$

$$h_1 q_1 = s(l-) - s_0, \quad (2.19)$$

where

$$h = \lambda/A, \quad h_0 = D_{ij} \dot{j} k_0, \quad h_1 = D_{ij} \dot{j} k_1, \quad (2.20)$$

and

$$u_0 = D \tau N_0, \quad s_0 = A \eta_0. \quad (2.21)$$

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\[
\cosh \left( l-x \right) = \frac{1}{\sinh l} \sum_{k=-\infty}^{\infty} \frac{1-ix_k \tanh l/2}{x_k^2 + 1} \exp (ix_k x) \quad (3.4b)
\]

\[
\cosh x = \frac{1}{\sinh l} \sum_{k=-\infty}^{\infty} \frac{1+ix_k \tanh l/2}{x_k^2 + 1} \exp (ix_k x) \quad (3.4c)
\]

and insert the expansions (3.1) and (3.2) into eqs. (2.14) and (2.15). Identifying coefficients of \( \exp (ix_k x) \) yields the linear system

\[
S_0 + U_0 \delta = u_0 (1 + \sigma) + Al/2, \quad (3.5a)
\]

\[
bS_0 + U_0 (1 + b\delta) = b [u_0(1 + \sigma) + Al/2 + (q_0 + q_i)/l], \quad (3.5b)
\]

\[
S_k (x_k^2 + 1) + U_k x_k^{-1} \tanh x_k \delta = iA/x_k, \quad (3.5c)
\]

\[
bS_k + U_k \left( 1 + \frac{b \tanh x_k \delta}{x_k} \right) = b \left[ \frac{iA}{x_k} + \frac{q_0 + q_i}{l(x_k^2 + 1)} + \frac{(q_i - q_0)ix_k \tanh l/2}{l(x_k^2 + 1)} \right], \quad (3.5d)
\]

which is readily solved. We get

\[
U_0 = \frac{(b/l)(q_0 + q_i)}, \quad (3.6a)
\]

\[
S_0 = u_0 (1 + \sigma) + Al/2 - (b\delta/l)(q_0 + q_i), \quad (3.6b)
\]

\[
U_k = bA_k^{-1} [ix_k A + l^{-1}(q_0 + q_i) + l^{-1}(q_i - q_0)ix_k \tanh l/2], \quad (3.6c)
\]

\[
S_k = [x_k (x_k^2 + 1)A_k]^{-1} \left( iA (x_k^2 + 1) - b \tanh x_k [l^{-1}(q_0 + q_i) + l^{-1}(q_i - q_0)ix_k \tanh l/2] \right), \quad (3.6d)
\]

where

\[
A_k = x_k^2 + b x_k \tanh x_k \delta + 1. \quad (3.7)
\]

Introducing the \( S_k \)'s into eq. (3.3) yields the constant \( A \) which is expressed as

\[
A/l = (q_i - q_0)T_1, \quad (3.8)
\]

where

\[
T_1 = \frac{b \tanh l/2 \sum_{k=1}^{\infty} (x_k^2 + 1)^{-1} A_k^{-1} \tanh x_k \delta}{1 + 2 \sum_{k=1}^{\infty} A_k^{-1}}. \quad (3.9)
\]

As predicted, eq. (3.8) shows that \( A \) depends on the difference of the currents. The same is true of the discontinuity of \( s(x) \) at a step, and is

\[
s(0 + ) - s(l - ) = (q_i - q_0) \tanh l/2 + A(l - (q_i - q_0) \tanh l/2 + 2T_1), \quad (3.10)
\]

according to eqs. (3.2) and (3.8). Thus for symmetric steps \( q_0 = q_i \), the density \( s(x) \) is continuous at steps and the constant \( A \) vanishes.

Finally, the currents \( q_0 \) and \( q_i \) are determined by the capture reactions (2.18) and (2.19). Using eqs. (3.6) and (3.8), we introduce the convenient abbreviation

\[
\sum_{k \neq 0} S_k = -(q_0 + q_i)T_0, \quad (3.11)
\]

where

\[
T_0 = (2b/l) \sum_{k=1}^{\infty} x_k^{-1}(x_k^2 + 1)^{-1} A_k^{-1} \tanh x_k \delta. \quad (3.12)
\]
Then, inserting the expansion (3.2) into eqs. (2.18) and (2.19), and noting eq. (2.17), we get the system

\[(h_0 + x)q_0 + \beta q_1 = \sigma u_0, \quad \beta q_0 + (h_1 + x)q_1 = \sigma u_0,\]

(3.13)

where

\[x = \coth l + h_0 + T_0 + T_1, \quad \beta = \csch l + h_0 + T_0 - T_1.\]

(3.14)

The linear system (3.13) then yields the currents

\[q_0 \sim \sigma u_0 \Delta^{-1} (h_1 + x - \beta), \quad q_1 \sim \sigma u_0 \Delta^{-1} (h_0 + x - \beta),\]

(3.15)

where

\[\Delta = (h_0 + x)(h_1 + x) - \beta^2.\]

(3.16)

We see that the currents are indeed equal when \(k_0 = k_1\) (or \(h_0 = h_1\)).

Reverting to dimensional variables (2.9)-(2.11) and (2.21), we derive expressions for the total current to a step and hence for the growth rate. First, using eqs. (3.14) and (3.15) we write the total current to a step in the form

\[o + j_1 = (D_j / \lambda \Delta)(q_0 + q_1) = j_{BCF} f(l/2\lambda, \delta / \Lambda, h, h_0, h_1),\]

(3.17)

where the BCF current to an isolated step

\[j_{BCF} = 2\pi \sigma D N_0 / \Lambda = 2\pi \sigma n_0 / \tau\]

(3.18)

is modulated by the function

\[f \equiv \frac{1}{2} (h_0 + h_1) + \tanh (\frac{1}{2} / \lambda) + 2T_1\]

\[= \frac{1}{2} (h_0 + h_1) + \tanh (\frac{1}{2} / \lambda) + 2T_1 + \coth (\frac{1}{2} / \lambda) + (\delta / \Lambda) (2\lambda / l + 2T_0) - \frac{1}{2}(h_0 - h_1)^2.\]

(3.19)

The second equality in eq. (3.18) results from the equilibrium condition (2.5), and we recall the definition (2.20) of the \(\delta\)'s appearing in eq. (3.19). Now it is well known that the growth rate \(R\) of the crystal is related to the total current according to

\[R = (\Omega / l)(j_0 + j_1),\]

(3.20)

where \(\Omega\) is the volume of a growth unit in the crystal. Using eqs. (3.17)-(3.20) we obtain

\[R = R_1 (l/2\lambda)^{-1} f = R_M (1 + \delta / \Lambda) (l/2\lambda)^{-1} f.\]

(3.21)

where

\[R_1 = \Omega \sigma D N_0 / \Lambda = \Omega \sigma n_0 / \tau\]

(3.22)

is the maximum growth rate obtained in the BCF theory, and where

\[R_M = \Omega \sigma N_0 D (\delta + \Lambda) = R_1 (1 + \delta / \Lambda).\]

(3.23)

is the most general expression for the maximum growth rate when volume rate limitations are considered. The value \(R_M\) is attained when steps are close enough the permit all of the atoms impinging on the crystal surface to equilibrate with steps. In fact, it is easy to see from eq. (3.19) that, as \(l \to 0\), the modulating function \(f\) behaves as \((1 + \delta / \Lambda)^{-1} (l/2\lambda)\). The rate limitations associated with \(R_M\) are due to diffusion through the stagnant layer and to adsorption kinetics, and are represented by the impedances \(\delta / D\) and \(\Lambda / D\) respectively. We see that \(R_M\) tends towards \(R_1\) when \(\delta \ll \Lambda\), i.e., when volume diffusion is fast compared to adsorption kinetics. Expressions such as (3.23) for the growth rate are well known in the literature, they have been analyzed by Brice in detail. Notice that the total current (3.17) and the growth rate (3.21) depend on the supersaturation \(\sigma\) in two ways. Firstly, \(j_{BCF}\), \(R_1\) and \(R_M\) are all linear in \(\sigma\) as required by the linearity of the governing equations. Secondly, the
distance between steps $l$ can depend on $\sigma$ because, in the case of a dislocation mechanism for step production, the arms of the spiral wind more tightly around its dislocation core when $\sigma$ is increased. This leads to a $l(\sigma)$ relationship proposed by BCF$^2$) and later refined by Cabrera and Levine$^{20}$),

$$2l/\sigma = \sigma/\sigma_1,$$  \hspace{1cm} (3.24)

where $\sigma_1$ depends on such physical parameters as the number of cooperating screw dislocations, the edge free energy of a nucleus, and the temperature. Finally, we note that the modulating function $f$, eq. (3.19), and therefore the growth rate (3.21), is symmetric in $h_0 = D_s/\lambda k_0$ and $h_t = D_s/\lambda k_t$. This means that our model does not distinguish the positive from the negative $x$-direction. From a fundamental point of view, the governing equations (2.1)-(2.8) are invariant under the spatial inversion $x \to -x$, because we neglect the motion of the step during the diffusion process. This symmetry is broken if one considers the explicit motion of the step$^{11}$).

4. Current to an isolated step

In section 5 we shall see that almost all the information concerning growth rates under low supersaturations can be inferred from the behavior of the surface current to an isolated step. Therefore, in this section we examine the diffusion fields and currents due to such a step in some detail. They are obtained from the expressions of the previous section in the limit $l \to \infty$.

First, we consider the limiting cases of "symmetric" and "asymmetric" currents. The symmetric condition is calculated for equal capture kinetics on both sides of the step, i.e., $k_0 = k_t = k$, ($h_0 = h_t = h$); the asymmetric condition corresponds to the case of given kinetics on the right and slow kinetics on the left of the step, i.e., $k_0 = k$ ($h_0 = h$) and $k_t \to 0$ ($h_t \to \infty$). The first condition implies equal currents from the right and left of the step; the second implies that the current from the left, $j_l$, is zero (the left side is blocking), and that all the current must come from the terrace to the right of the step. Using eqs. (3.17) and (A.17)-(A.18) of Appendix A, we obtain these currents in the form:

$$j_{s\text{ym}}/j_{\text{BCF}} = (h + 1 + 2T_0)^{-1},$$ \hspace{1cm} (4.1)

$$j_{a\text{sym}}/j_{\text{BCF}} = \frac{1}{2} (h + 1 + T_0 + T_1)^{-1}.$$ \hspace{1cm} (4.2)

The values for $T_0$ and $T_1$ are computed according to (A.3)-(A.4). In the remainder of this section we will discuss the currents (4.1)-(4.2) for the case of fast capture kinetics, $k \to \infty$ ($h = 0$). The effect of finite values of the reaction constants $(k_0, k_t)$ is deferred to the next section. Some of the following results for $j_{s\text{ym}}$ have been presented in I.

The current $j_{s\text{ym}}$ is given in fig. 2 for a wide range of values of the coupling parameter $b = \lambda/\Lambda$ and for various values of $\delta/\Lambda$. In all cases, increasing $b$ clearly increases the current to the step. We note that the BCF current (3.18) is proportional to $b$: it is the maximum available current to an isolated step. There are three distinct regions of these curves which show up clearly when, for example, $\delta/\Lambda = 10^4$. The "BCF regime" occurs for $b < 10^{-1}$; here the current $j_{s\text{ym}}$ is closely approximated by the BCF current. In the range $10^{-1} < b < (\delta/\Lambda)^{\frac{1}{3}} = 10^2$ the current for $\delta/\Lambda = 10^4$ moves away sublinearly from $j_{\text{BCF}}$. We call this range the "cylindrical volume diffusion regime" for reasons which will become apparent later. Finally, for $b > (\delta/\Lambda)^{\frac{1}{3}} = 10^2$, $j_{s\text{ym}}$ is again linear in $b$ but remains two orders of magnitude smaller than $j_{\text{BCF}}$. This we call the "planar volume diffusion regime". The three regions are also apparent in fig. 3, where $j_{s\text{ym}}$ and $j_{a\text{sym}}$ are directly compared to $j_{\text{BCF}}$. We will now discuss these regions in more detail.

4.1. The BCF regime: $b < 10^{-1}$

The effect of a finite volume diffusion rate is very small and $j_{s\text{ym}}$ reduces to $j_{\text{BCF}}$ according to the estimates (A.12)-(A.13). This result is expected since a small surface mean diffusion distance $\lambda$ and a large surface-volume exchange impedance $\Lambda$ both make it very difficult for the growth units in the volume to reach the step. Therefore
the current to the step is small, and can have very little impact on the volume density of growth units. This density must then be approximately equal to \( N_0 (1 + \sigma) \) maintained at the top of the unstirred layer, i.e., the conditions assumed by BCF are then valid. The asymmetric current \( j_{\text{asym}} \) is then obviously half the symmetric current since the step receives growth units from the right only. We emphasize that these results apply only to the case of an isolated step. A series of parallel and closely spaced steps can cause a large reduction of the volume density near the surface, and the currents may be several orders of magnitude less than the BCF prediction, even when \( b \) is small. This effect will be treated in section 5.

4.2. CYLINDRICAL VOLUME DIFFUSION REGIME: \( 10^{-1} < b < (1 + \delta/A)^2 \)

When \( b \equiv \lambda/A \leq 1 \), \( j_{\text{sym}} \) falls significantly below \( j_{\text{BCF}} \), the drop being more pronounced for large values of \( \delta/A \). This drop implies that volume density gradients are present. These cause a reduction in the density of growth units adjacent to the surface, a large value of \( \delta \) allowing a large reduction to occur. The large volume gradients are caused by the large surface currents flowing to the step. As discussed in Appendix B, when \( b \gtrsim 1 \), eq. (2.15) shows that the volume density adjacent to the surface must be approximately proportional to the surface density. Such a situation has been called the "proportional disturbance" regime\(^\text{21} \) and marks the transition from the BCF regime to the cylindrical volume diffusion regime.

Further insight can be gained by examining the volume diffusion fields. Figs 4 and 5 show diffusion flux lines obtained by a Runge–Kutta numerical integration procedure of

\[
\frac{dx}{dy} = \frac{\partial u}{\partial x}, \frac{\partial u}{\partial y},
\]

in which the series expansion (3.1) for \( u(x,y) \) is transformed into an integral, as in Appendix A. The flux lines are represented for the case of asymmetric capture conditions \( (k_0 \rightarrow \infty, k_1 \rightarrow 0) \) and for \( \delta/A = 10^{-3} \). Thus one expects some skewness in the diffusion flow patterns and marked curvature due to volume gradients. The flux lines in fig. 4 when \( b \equiv \lambda/A = 1 \) are almost identical to those obtained for smaller values of \( b \). We note that the asymmetric capture conditions are not reflected in the diffusion field on the macroscopic scale of fig. 4 (distances are measured in units of \( \delta \)). This is not surprising since the catchment area \( 2\lambda \) of the step (cf. Appendix B) is small in comparison with \( \delta (\lambda/\delta \approx 10^{-3}) \). Again, the scale of the figure shows an approximate cylindrical symmetry around a step (which justifies the name given to this range of \( b \)-values), although one can easily show (cf. 1, p. 83) that...
such a symmetry can never be strictly attained. This range of $b$-values represents those conditions under which Chernov's approximate volume diffusion model holds. The flux lines in fig. 4 are nearly identical to the electric field lines of force between two equipotential capacitor plates at $y = \pm \delta$ and a charged line at $x = y = 0$. We see that a step can "funnel" growth units from large regions of the unstirred layer because volume gradients can extend over regions of the order $\delta$, or more. Thus we expect a step to have a long range effect on distant steps, because their associated funnels can interfere. Increasing the value of $\lambda$ in the region $\lambda \leq \Lambda$ does not affect the geometry of the pattern but has the very important effect of increasing the strength of the sink, i.e. the density of isoconcentration lines around the step is increased and large $x$- and $y$-gradients are set up.

### 4.3. Planar Volume Diffusion Regime: $b > (1 + \delta/\Lambda)^{\frac{3}{2}}$

For such large values of $b \equiv \lambda/\Lambda$, the currents go to the limiting values

$$j_{\text{sym}}/j_{\text{BCF}} = 2 j_{\text{asym}}/j_{\text{BCF}} = (1 + \delta/\Lambda)^{-\frac{3}{2}},$$

where expressions (A.15) have been used. The reasons for $j_{\text{asym}}$ being again half of $j_{\text{sym}}$ will be discussed later.

Fig. 5 shows the flow pattern when $\lambda/\Lambda = 100$. It is clear that the large surface current has caused a distinct change in the geometry of the diffusion field. Firstly, the absence of a surface current to the left of the step is apparent because the flux lines originating on the left are bending over to terminate on the right side. Thus one can expect an enhancement of the current $j_{\text{sym}}$ since it is fed by volume regions ($x < 0$) to the left of the step. Secondly, the extreme asymmetry of the volume density around the step is illustrated by a dashed isoconcentration line. Thirdly, the extent of the surface diffusion field (the catchment area, cf. Appendix B) is large since flux lines terminate far to the right of the step. In Appendix B, we prove that the catchment area for $b > (\delta/\Lambda)^{\frac{3}{2}}$ has increased dramatically and is of the order $2(\delta/\Lambda)^{\frac{3}{2}}\lambda$; it corresponds to $x \approx 3\delta$ for the case sketched in fig. 5. This range of $b$-values represents the conditions under which a "Volmer layer" is established. Finally, we note that the flux lines in fig. 5 are analogous to the electrical lines of force between two infinite equipotential capacitor plates located at $y = \pm \delta$ and a charged semi-infinite plate located at $y = 0, x \geq 0$. This justifies the name given to the range of $b$-values.

The effect of surface currents on volume gradients can be estimated by introducing an effective diffusion width $W_D$, defined by Queisser, Huber and Shockley as

$$W_D \equiv D_n n_0/D N_0 = \frac{\lambda^2}{\Lambda},$$

where the last equality results from eq. (2.5) and the definition (2.10) of $\lambda$. Physically, $W_D$ is the thickness of a slab of fluid required to carry the same diffusion current as the surface current under equivalent conditions. The term $n_0/N_0$ in the definition accounts for any tendency of the growth units to segregate on the surface as a result of
atomic forces. The ratio of the effective diffusion width to the thickness of the unstirred layer.

$$W_D/\delta = (\lambda/\Lambda)^2 (\Lambda/\delta) - h^2 (\delta/\Lambda)^{-1}.$$  \hspace{1cm} (4.6)

is of primary importance. When $W_D \ll \delta$, which occurs when $b \ll (\delta/\Lambda)^{1/2}$, the current that the surface can carry is small in comparison with the volume flux which can be handled by volume regions of width $\delta$. This implies that appreciable gradients in the volume density must be limited to regions close to the step. When $W_D/\delta \simeq 0.1$ the volume density is reduced over a region comparable to, but less than the available volume $\delta$, causing a reduction of the surface currents relative to $j_{BC1}$ as evidenced in figs. 2 and 3. Finally, when $W_D \simeq \delta$, there is an impedance match between volume and surface diffusion; the surface draws the maximum available flux from a region of radius $\delta$ surrounding the step. In view of eq. (4.6) this condition can be expressed as

$$b = \lambda/\Lambda \simeq (\delta/\Lambda)^{1/2},$$  \hspace{1cm} (4.7)

and gives that value of $b$ in figs. 2 and 3 where the currents attain their asymptotic values (4.4). For example, in fig. 3 the $\delta/\Lambda = 100$ curves are within $10\%$ of their asymptotic values at $b = 10$. With thicker unstirred layers, the asymptotic value is approached for larger $b$'s according to eq. (4.7). Physically, when $W_D > \delta$, the surface current becomes so large that, in order to supply it, the extent of the volume diffusion region must spread laterally beyond a distance $\delta$. The volume and surface fields are then so strongly coupled that the volume density $N(x,0)$ must be strictly proportional to the surface density $n(x)$.

The volume phase allows the currents on either side of a step to interfere. The ratio $j_{asym}/j_{sym}$ in fig. 6 reveals this effect very clearly if we think of $j_{sym}$ as being composed of two asymmetric currents. For small values of $b \equiv \lambda/\Lambda$, this ratio is one half, since then the volume density is approximately constant, and blocking the current to the left can have no effect on that part of $j_{sym}$ which comes from the right. However, when $b = \lambda/\Lambda \approx 1$, the build-up in $x$-gradients causes $j_{sym}$ to increase more slowly than $j_{asym}$ since, in the asymmetric case, the current to the right of the step can be fed from volume regions on the left. Volume diffusion is then an important rate limitation and causes interference because the terraces to the right and left of the step compete for the available flow of growth units from the volume. For example, fig. 6 shows that, for $\delta/\Lambda = 10^5$ and $\lambda/\Lambda \approx 30$, blocking one side of a step causes only a $6\%$ reduction from the current available under symmetric capture conditions. For yet larger values of $\lambda/\Lambda$, at first sight it appears paradoxical that the ratio $j_{asym}/j_{sym}$ should fall back to one half. However from fig. 5 we see that relatively few flux lines cross over from the left to terminate on the right of the step and that the lines on the right can terminate far from the step. Thus one is comparing a relatively small amount of “cross over” contribution to the current with a large component from the right side of the step.

---

Fig. 6. Ratio of the asymmetric to the symmetric current to an isolated step versus the coupling parameter $b$, for various values of $\delta/\Lambda$.

Fig. 7. Normalized growth rate versus step density (or supersaturation). The initial slope defines the interaction distance (or the critical supersaturation), and determines the extent of parabolic growth kinetics.
We can summarize this section as follows: when \( b \equiv \lambda/A \lesssim 10^{-1} \) (BCF regime), there are insignificant volume density gradients regardless of the thickness of the unstirred layer; as \( b \) increases in the range \( 10^{-1} \lesssim b \leq (1 + \delta/|A|)^{1/2} \) (cylindrical volume diffusion regime), appreciable \( x \)- and \( y \)-gradients can be set up, and a large drop in the volume density results when \( \delta/|A| > 1 \); when \( b > (1 + \delta/|A|)^{1/2} \) (planar volume diffusion regime), there can be large \( y \)-gradients, but \( x \)-gradients are small except near the step in the case of asymmetric capture conditions (the \( x \)-gradients are everywhere small for symmetric conditions).

5. Discussion of the growth rate

Fig. 7 shows a typical relation between the growth rate \( R \) and the step density \( \ell^{-1} \), as calculated with the general formulas (3.21) and (3.19). The linear behavior for low step density and the asymptotic approach to a maximum \( R_M \) at high step density are general features. In view of eqs. (3.24) and (3.23), the step density and \( R_M \) are both proportional to the supersaturation \( \sigma \). We emphasize that the linear part of fig. 7 corresponds to the parabolic growth law \( R \propto \sigma^2 \) when a dislocation mechanism is operative. In that case, curves similar to fig. 7 also represent \( R/\sigma \) versus \( \sigma \).

Fig. 7 suggests the introduction of a critical distance \( l_c \) between steps and defined by

\[
l_c = \lim_{l \to 0} \frac{dR}{R_M} \frac{d(l^{-1})}.
\]

It is proportional to the initial slope of fig. 7, and measures significant departures from linearity when \( l \approx l_c \). In terms of the supersaturation, the extent of the parabolic growth regime is measured by a critical supersaturation \( \sigma_c \) defined, in view of eq. (3.24), by

\[
\sigma_c/\sigma_1 = 2l_c/\lambda_c.
\]

Generally, \( \sigma \approx \sigma_c \) determines the transition between parabolic \( (\sigma < \sigma_c) \) and linear \( (\sigma > \sigma_c) \) growth laws. The existence of a linear region in the \( R(l^{-1}) \) curve when \( l > l_c \) (or \( \sigma < \sigma_c \)) implies that the total current to steps is then roughly independent of \( l \). This is most easily seen from eq. (3.20) relating \( R \) to \( j_0 + j_1 \) and can be proven analytically. Furthermore, since one remains in the linear region as \( l \to \infty \) [case 1 of Cabrera and Coleman\textsuperscript{23}], this total current must be approximately equal to the total current to an isolated step. Thus, in the linear region, volume and surface diffusion processes to neighboring steps do not interfere, and \( l_c \) can be interpreted as the separation where neighboring steps begin to compete for the available input of growth units from the top of the unstirred layer. When \( l \approx l_c \) \((\sigma \approx \sigma_c)\) the entire surface is a sink and the growth rate approaches \( R_M \). Using eqs. (5.1), (3.21), and (3.17), we see that \( l_c \) is given by

\[
\frac{l_c}{2\lambda} = \left(1 + \frac{\delta}{\lambda} \right) \lim_{l \to \infty} \frac{j_0 + j_1}{j_0 + j_1 \text{BCF}}.
\]

Thus, \( l_c \) is proportional to the total current to an isolated step, a situation which was discussed in the last section. Fig. 8 shows the behavior of \( l_c/2\lambda \) as a function of \( b \equiv \lambda/A \). The symmetric case \((k_0 = k_1 \to \infty, \text{ both sides of the step at equilibrium and receiving equal currents})\) is represented by full lines; the asymmetric case \((k_0 \to \infty, k_1 \to 0, \text{ right side at equilibrium, left side blocking})\) is represented by dashed lines. The curves are calculated from eqs. (5.3) and (A.19) in which we set \( h = 0 \). These curves are obviously similar to those of fig. 2 since \( l_c \propto j_0 + j_1 \); however we will now interpret them differently. The BCF theory interprets \( 2\lambda \) as the catchment area per unit length of a step. The catchment area is a strip bordering the step within which the surface currents are large (i.e. the surface density is rapidly varying). Thus, a pair of steps within a distance \( 2\lambda \) will interact, causing a reduction in the growth rate. Similarly, in our more general picture of coupled volume and surface rate limitations, \( l_c \) can be viewed as the interaction distance of a pair of steps. This does not imply that surface densities vary quickly within a strip of width \( l_c \) around a step; volume gradients alone can produce a funneling pattern (cf. fig. 4) over each step and these funnels of width \( l_c \) can interfere. In fact for small values of \( h \), Appendix B shows that the width
Fig. 8. Interaction distance between steps relative to its BCF value versus the coupling parameter $h$, for various values of $\delta/A$ and for fast attachment kinetics to the right of steps. Full (dashed) curves represent symmetric (asymmetric) capture conditions.

Fig. 9. Effect of finite attachment kinetics to the right of steps on the relative interaction distance versus the coupling parameter $h$, for various values of $k_0$. Full (dashed) curves represent symmetric (asymmetric) capture conditions.

of appreciable surface gradients is still $2\lambda$, although fig. 8 demonstrates that $l_c$ can be orders of magnitude larger. Thus we interpret $l_c/2\lambda$ in fig. 8 as the change in the interaction distance when compared to its BCF value. In view of eq. (5.2) this ratio also measures the change in the extent of the parabolic region $\sigma_c$ over its BCF value $\sigma_1$. The unstirred layer thickness $\delta$ has a dramatic effect on $l_c$. In fact for small values of $h = \lambda/A$, $l_c$ is proportional to $(1+\delta/A)$, but for $h \geq (\lambda/A)^3$ it is proportional to $(1+\delta/A)^{3/2}$ in accordance with eqs. (5.3) and (A.19). We emphasize that $l_c$ increases with $\delta/A$ and therefore the extent of the parabolic region, $\sigma_c \propto l_c^{-1}$, decreases. As we pointed out in I, the parabolic region can be several orders of magnitude smaller than that ($\sigma_1$) predicted by the BCF theory. For a given value of $\delta/A$, increasing $h = \lambda/A$ tends to increase the parabolic region above its extent estimated for $h = 0$, the increase being $(1+\delta/A)^{3/2}$ at most. Fig. 9 shows the effect of finite reaction kinetics at steps. Full curves represent again the symmetric case, $k_0 = k_f = k$, and the dashed lines correspond to the asymmetric case, $k_0 = k_f = 0$. Here we point out that $\sigma_c \propto l_c^{-1}$ increases above its BCF value $\sigma_1$ when $h^{-1} = k_1/D_c$ decreases below $\delta/A$. Again, $\sigma_c$ increases with $h$ although this effect is small when $k_1/D_c \leq \lambda/\delta$. Finally, from both figs 8 and 9, we see that for a given value of $\delta/A$ and $h$, asymmetric conditions can, at most, double the parabolic region over the one estimated for symmetric conditions.

In figs. 10 and 11, the growth rate $R$ versus step density is compared to $R_1$, its maximum value allowed by the BCF theory. We represent the case $h = \lambda/A \to 0$ only. In fig. 10, we note that $R_M$ and $\sigma_c$ are strongly affected by $\delta/A$; they are roughly inversely proportional to $\delta/A$, in accordance with eqs. (3.23), (5.2) and (5.3). Thus, for $\delta/A = 10$, $R_M$ and $\sigma_c$ are approximately ten times smaller than for $\delta/A = 0$. Asymmetric conditions somewhat increase the extent of the parabolic region $\sigma_c$ but do not affect $R_M$. Fig. 11 shows that the growth rate for $k_0 = k_f = 0.1 D_c/\lambda$ is reduced by a factor of ten from the BCF result for low step density. However, the extent of the parabolic region $\sigma_c$ is increased in that proportion. In fact, for $h \to 0$ and for low step density, it is easy to see that the growth rate behaves as

$$R \approx R_1 (2\lambda/l) \frac{1}{2} [(1 + D_c/\lambda k_0)^{-1} + (1 + D_c/\lambda k_f)^{-1}].$$

Therefore in this low step density region (parabolic region), $R$ is reduced by a factor $h_0 \equiv D_c/\lambda k_0$ or $h_1 \equiv D_c/\lambda k_f$. 

$$R \approx R_1 (2\lambda/l) \frac{1}{2} [(1 + D_c/\lambda k_0)^{-1} + (1 + D_c/\lambda k_f)^{-1}].$$
whichever is larger, relative to the BCF behavior \( R_1 \) \((2/\delta)\). \( \sigma_c \) is increased by a factor \( h_0 \) or \( h_1 \), whichever is smaller, relative to its BCF value \( \sigma_1 \). Again, finite attachment kinetics do not affect \( R_M \), and asymmetric conditions somewhat increase \( \sigma_c \).

6. Summary and conclusions

We have solved the coupled volume and surface diffusion problem associated with an unstirred fluid layer adjacent to a growing, stepped, crystal surface. In particular, we have extended our earlier results, I\(^{10}\), to the case when steps allow different capture rates for growth units arriving from the upper or the lower terrace. In our model we can distinguish four classes of physical parameters:

1. Those, \( \delta \) and \( D \) relating to the volume phase alone.
2. Those, \( \lambda \) and \( A \), describing volume–surface interactions.
3. Those, \( k_0 \) and \( k_1 \), controlling the departure of the surface density from its equilibrium value.
4. The distance \( l \) between steps, which is determined by the supersaturation in the case of a dislocation growth mechanism.

We note that the parameters \( D_s \) and \( \tau \) cannot be obtained from growth rate experiments since they only occur as the combination \( \lambda \) in the expression of the growth rate. However, monitoring the adsorbed surface density would yield separate estimates for \( D_s \) and \( \tau \).

The rate limitations on the overall growth process depend on the ratios of the aforementioned parameters. The ratio \( D/\delta \) controls the maximum rate at which growth units can be supplied from the volume phase. However, this maximum rate is not achieved because of adsorption kinetics (measured by the ratio \( \delta/\lambda \)), and because of finite rates of capture at steps (measured by the ratios \( h_0 \equiv D_s/\lambda k_0 = \lambda/\tau k_0 \) and \( h_1 \equiv D_s/\lambda k_1 = \lambda/\tau k_1 \)). These “branching” ratios measure the relative importance of adsorption kinetics on terraces to volume diffusion, and of capture kinetics at steps to surface diffusion respectively. The first ratio is more obvious if we remember that the adsorption rate constant [eq. (2.3)] was defined as \( K \equiv D/\lambda \). Therefore, \( \delta/\lambda = \delta K/D \) is the ratio of the reaction rate \( K \) to the rate of volume diffusion \( D/\delta \). The ratio \( b = \lambda/\Lambda \) is a coupling constant since it controls the magnitude of the volume gradients due to surface processes. Increasing \( b \) always increases the current to steps although this effect is small when the \( k \)'s are small and when the steps are close together. In fact, neither \( b \), nor the \( k \)'s affect the maximum growth rate \( R_M \) obtained when \( l \to 0 \), although they do control how quickly \( R_M \) is approached. For
very large $b$'s [$b \gg (\delta/A)^3$], the surface density $n(x)$ is constrained to be proportional to the adjacent volume density $N(x,0)$. This law of proportional disturbances\textsuperscript{21} is often quoted in grain boundary diffusion problems. Under such conditions the surface density varies extremely slowly. Then, the extent of significant surface gradients, i.e., the catchment area, is $2\lambda(1+\delta/A)^3$, and can be orders of magnitude larger than its BCF estimate $2\lambda$. The effective diffusion width $W_D = \lambda^2/A$ estimates the extent of perturbed volume regions. Appreciable volume gradients extend within a distance $W_D$ of an isolated step. These gradients are necessary to supply the surface currents to steps. Finally, allowing for unequal capture rates, $k_0 \neq k_f$, implies that flux lines can cross normal planes to the surface along steps, thus yielding an interference effect between the currents on either side of a step.

From the point of view of experiment, we showed that, in the case of a dislocation mechanism, $R/T$ versus $T$, curves should begin to rise linearly and then reach a plateau $R_m$ (fig. 7). The initial slope is related to the critical supersaturation $\sigma_c$ which measures the extent of the "parabolic growth law" and is inversely proportional to the critical distance $l_c$ at which neighboring steps begin to compete. Brice\textsuperscript{15} has shown how $R_m$ can be analyzed to give $D$ and $A$ if the degree of fluid stirring, which determines the stagnant layer thickness $\delta$, can be controlled. Furthermore if the initial slope ($\propto \sigma_c^{-1}$) varies with stirring, we can state the following:

1. $\sigma_c \propto (1+\delta/A)^{-1}$ indicates that $b < 1$.
2. $\sigma_c \propto (1+\delta/A)^{-2}$ indicates that $b > (1+\delta/A)^3$.
3. $\sigma_c$ does not vary with $\delta$ indicates that capture kinetics are sluggish and that the $(D_0/k)$'s are certainly larger than $\delta/A$. If sufficiently precise temperature dependent determinations of $R_m$ and $\sigma_c$ are possible, we generally do not expect a single activation energy. We note that the $k$'s and $A$ depend on the solvent. In fact, for vapor growth, $A$ is approximately the mean free path, and should be inversely proportional to the total gas pressure and to the collision cross section. One could imagine controlled growth experiments in which growth rates under otherwise equal conditions are measured before and after the introduction of some "poison". This would tend to lower the rates $k_0$ and $k_f$, thus expanding the parabolic region, but should not affect the maximum growth rate $R_m$ at high supersaturation.

Finally, the results of sections 4 and 5 are relevant to the question of the stability of a series of parallel steps to perturbations in the spacing. In this paper we have assumed an equidistant spacing in all calculations of the growth rate; if the steps move out of this arrangement, this will affect the growth rate and give a nonuniform surface morphology. In the presence of negligible volume diffusion gradients, perturbations either increase or decay in amplitude, the result depending on the capture kinetics at the step\textsuperscript{14,15}. The step train is stable when the capture kinetics in front of a moving step are faster than those behind it. In this case, a step which happens to move ahead of the equidistant position, for example, will experience a reduction in its current. This occurs because of the decrease in the size of the terrace in front which supplies the major portion of the current. The reduced current causes a decrease in step velocity and tends to restore the step to its equidistant position; therefore stability is assured. When the kinetics behind the step are faster, a step moving ahead experiences an increased velocity as a result of this move and therefore goes even farther out of position. In this case the system is unstable, and perturbations tend to grow. These results apply when the distance between steps is less than the catchment area, or $l \leq 2\lambda$ in this case, since only then will the motion of the step be affected by the positions of its neighbors.

It is apparent from the results of section 4 that volume density gradients can greatly extend the distance over which neighboring steps may influence one another. This implies that stability effects are possible at distances much greater than $\lambda$, although they may be very weak. The rate of decay or growth of perturbations will probably be rather small in the BCF or cylindrical symmetry regimes since the volume diffusion field is nearly symmetric, even with asymmetric capture probabilities. This is true at large step separation when only the volume fields overlap, but when the steps approach a distance $2\lambda$ the situation should be quite similar to that discussed above in the absence of volume gradients. In the planar diffusion regime, very strong stability effects are expected with asymmetric capture conditions as a result of the asymmetric volume and surface diffusion fields. Also, the stability effects should extend to very large step spacings because of the large lateral extent $l_c$ of the diffusion field. A quantitative evaluation of the effect of volume diffusion on step stability requires a solution of the diffusion
equations for a series of parallel steps which are perturbed from an equidistant spacing; only from such a solution
can the rate of growth or decay of the perturbation be obtained.

Appendix A. The limit of widely spaced steps

We discuss the behavior of the series $T_0$ and $T_1$ when $l \gg \lambda$. These series then go over into integrals in a way
which can best be described with Poisson’s sum formula\(^2^4\). This formula transforms sums of sufficiently regular
functions $\phi(z)$ into sums of its Fourier transform:

\[
\sum_{k=-\infty}^{\infty} \phi(k) = \sum_{n=-\infty}^{\infty} \int_{-\infty}^{\infty} dt \phi(t) \exp\left(-2i\pi nt\right).
\]  

Since all the functions appearing in $T_0$ and $T_1$ depend on the argument $z_k = 2\pi k/l$, the sum formula (A.1) can also be written

\[
\sum_{k=-\infty}^{\infty} f(z_k) = \left(\frac{l}{2\pi \lambda}\right) \int_{-\infty}^{\infty} dz f(z) + \left(\frac{l}{2\pi \lambda}\right) \sum_{n \neq 0} \int_{-\infty}^{\infty} dz f(z) \exp\left(-inz/l\right),
\]  

where $\phi(z) = f(2\pi z/l)$ and where the $n = 0$ term has been isolated. Now, it is easy to see that all the functions in
$T_0$ and $T_1$ have no real poles. Thus the Fourier integrals in the second term of the r.h.s. of (A.2) yield exponentially
small terms in $(l/\lambda)$ when evaluated with the residue theorem. It follows that, asymptotically, when $l \gg \lambda$,

\[
\pi T_0 \sim \int_{0}^{\infty} \frac{dz}{\lambda(\lambda^2 + 1)} \Delta(z) = \int_{0}^{\infty} \frac{dz}{\Delta(z)} + \int_{0}^{\infty} \frac{b \tanh \alpha \lambda}{\alpha(\lambda^2 + 1)} \Delta(z) - \frac{\pi}{2},
\]  

\[
2T_1 \sim \left[\int_{0}^{\infty} \frac{dz}{\lambda(\lambda^2 + 1)} \Delta(z) \right]^{-1} \left[\int_{0}^{\infty} \frac{dz}{\Delta(z)} \right]^{-1} = \frac{\pi}{2} \left[\int_{0}^{\infty} \frac{dz}{\Delta(z)} \right]^{-1} - 1,
\]  

where we define

\[
\Delta(z) = \lambda^2 + 2b \lambda \tanh \alpha \lambda + 1,
\]  

and use the identity

\[
\frac{b \tanh \alpha \lambda}{\lambda(\lambda^2 + 1)} \frac{x + b \lambda \tanh \alpha \lambda}{\lambda^2 + 1} = \frac{x}{\Delta(z)}
\]  

for the second forms of (A.3) and (A.4).

We now examine the behavior of $T_0$ and $T_1$ in the cases of small and large values of the coupling parameter
$b \equiv \lambda/\Lambda$. First we note the identity

\[
\delta \lambda = (\delta/\Lambda) b^{-1}.
\]  

This discussion assumes that $\delta/\Lambda$ is finite and non-zero since this parameter measures the relative importance of
volume diffusion to the adsorption reaction. Therefore, when $b \ll 1$, eq. (A.7) indicates that $\delta \lambda$ is very large and,
to first order in $b$, eqs. (A.3) and (A.4) are

\[
\pi T_0 \approx \int_{0}^{\infty} \frac{dx}{x^2 + bx + 1} + b \int_{0}^{\infty} \frac{dx \tanh \alpha \lambda}{\alpha(\lambda^2 + 1)} = \frac{\pi}{2},
\]  

\[
2T_1 = \frac{\pi}{2} \left[\int_{0}^{\infty} \frac{dx}{x^2 + bx + 1} \right]^{-1} - 1.
\]  

But

\[
\int_{0}^{\infty} \frac{dx}{x^2 + bx + 1} = \frac{2}{(4 - b^2)^{1/2}} \tan^{-1}\left(\frac{2 - b^2}{b}\right) \approx \frac{1}{2}(\pi - b),
\]  

(A.10)
\[\int_0^\infty \frac{\tanh x \delta/\lambda}{x(\lambda^2 + 1)} \, dx = \psi\left(\frac{1}{2} + \frac{\delta}{\pi \lambda}\right) - \psi\left(\frac{1}{2}\right) \approx \ln\left(1 + 2\delta/\pi \lambda\right) + \ln \frac{1}{2} - \psi\left(\frac{1}{2}\right), \quad (A.11)\]

where the asymptotic expression of the \(\psi\) function has been used. Inserting eqs. (A.10) and (A.11) into eqs. (A.8) and (A.9) yields

\[T_0 \approx (b/\pi) \left[\ln \frac{1}{2} - \psi\left(\frac{1}{2}\right) - \frac{1}{2} + \ln \left(1 + 2\delta/\pi \lambda\right)\right] \approx (b/\pi) \left[0.42 + \ln \frac{\delta}{\lambda}\right], \quad (A.12)\]
\[T_1 \approx b/2\pi. \quad (A.13)\]

Thus \(T_0\) and \(T_1\) are of order \(b\) and go to zero in the case of small surface-volume coupling.

On the other hand, for large values of \(b\), using eq. (A.7),

\[b \tanh \frac{\delta\lambda}{\lambda} \approx \frac{b \delta}{\lambda}\]

must hold over any significant portion of the interval of integration. The integrals (A.3) and (A.4) can then be performed exactly and we easily get

\[T_0 = T_1 = \frac{1}{2} \left[(1 + \delta/A)^{\frac{1}{2}} - 1\right]. \quad (A.15)\]

Thus, for strong coupling, the behavior of \(T_0\) and \(T_1\) depends essentially on the ratio \(\delta/A\).

For convenience, we record the expression of the modulating function (3.19) when \(I \gg \lambda\):

\[f = \frac{1}{2}(h_0 + h_1) + 1 + 2T_1 \quad \left[\frac{1}{2}(h_0 + h_1) + 1 + 2T_0\right] - \left[\frac{1}{2}(h_0 - h_1)\right]^2 = h_0h_1 + (h_0 + h_1)(1 + T_0 + T_1) + (1 + 2T_0)(1 + 2T_1). \quad (A.16)\]

The symmetric and asymmetric conditions defined in section 4 then yield the expressions:

\[f_{\text{sym}} = (b + 1 + 2I_0)^{-1}, \quad h_0 = h_1 = h, \quad (A.17)\]
\[f_{\text{asym}} = \frac{1}{2} (h + 1 + T_0 + T_1)^{-1}, \quad h_0 = h, \quad h_1 \to \infty. \quad (A.18)\]

We note that \(f_{\text{sym}} = 2f_{\text{asym}}\) in the limit of both small and large \(b\). In fact, using eqs. (A.12), (A.13) and (A.15), we get

\[f_{\text{sym}} \approx 2f_{\text{asym}} \approx \begin{cases} (1 + h)^{-1} & \text{if } b \ll 1, \\ (h + (1 + \delta/A)^{\frac{1}{2}})^{-1} & \text{if } b > (\delta/A)^{\frac{1}{2}}. \end{cases} \quad (A.19)\]

Appendix B. Estimates of the catchment area

We define the catchment area as the strip on a terrace adjacent to a step where surface density gradients are significant. It is an important parameter because it (a) relates to the current at a step, and (b) affects the geometry of the volume diffusion field, since the flux lines terminating within the catchment area are most effective for the overall transport. In section 4 we showed that the effective diffusion distance \(W_D\) measured the extent of appreciable volume gradients. The BCF estimate of the catchment area follows when \(W_D < \lambda\), which implies \(b = \lambda/A < 1\) according to eq. (4.5). Volume gradients being negligible, eqs. (2.2)-(2.4) become

\[D_n \frac{d^2n}{dx^2} - n + \frac{D}{A} N_0(1 + \sigma) = 0, \quad (B.1)\]

or, using eqs. (2.5) and the definition (2.10),

\[\lambda^2 \frac{d^2n}{dx^2} - n + n_0(1 + \sigma) = 0. \quad (B.2)\]
The solutions of this equation proposed by BCF\(^2\)) must necessarily depend on the dimensionless variable \(x/\lambda\), regardless of the form of the boundary conditions. Therefore the catchment area is \(2\lambda\) for small \(b\)’s. On the other hand, when \(W_0 > \delta\), which implies that \(b = \lambda/A > (\delta/A)^1\) according to eq. (4.5), we showed that no further reduction in the currents due to volume processes was possible. For such large values of \(b\), eqs. (2.11) and (2.15) show that the condition of proportional disturbances\(^2\))

\[ u(x,0) \equiv s(x) \quad \text{or} \quad n(x) = (D\tau/A) N(x,0) \quad (B.3) \]

must hold. If we approximate the volume field by a linear change in density normal to the surface and neglect \(x\)-gradients, we obtain the flux

\[ D \frac{\partial N}{\partial y} \bigg|_{y=0} = D \frac{N_0(1+\sigma)-N(x,0)}{\delta}. \quad (B.4) \]

We insert eqs. (B.3) and (B.4) into eq. (2.2) to get

\[ (\lambda^2 \delta/\lambda) \frac{d^2 N(x,0)}{dx^2} - N(x,0) + N_0(1+\sigma) = 0. \quad (B.5) \]

Thus the solutions of this governing equation must scale like \(x/\lambda(\delta/\lambda)^1\) and the catchment area is \(2\lambda(\delta/\lambda)^1\) for large \(b\)’s. A more rigorous estimate follows from the approximation (A.14)-(A.15) applied to the exact solution (3.1), (3.2), (3.6), and leads to a catchment area \(2\lambda(1+\delta/\lambda)^1\); it reduces to the above estimate when \(\delta/\lambda > 1\).

References

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