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Step-boundary conditions for crystal growth from the vapor phase

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We formulate the Chernov radiation boundary condition (rbc) used to describe the adatom-step exchange kinetics in terms of a microscopic description requiring a single parameter, the step sticking coefficient S. Explicit expressions are obtained for the rbc rate parameters and the attachment and detachment currents in terms of S and the operating parameters. Fully absorbing steps are considered as a special case, and the nonzero adatom density at the step determined together with the conditions that must hold when this is the equilibrium concentration.

I. INTRODUCTION

A variety of approaches have been used to describe the growth of crystals on stepped surfaces including both computer simulations[1,2] and analytic atomistic models.[3,4] Earlier work was concerned with the conditions specific to chemical vapor deposition (CVD), low-volume phase supersaturation, high temperature, and equilibrium or near-equilibrium steps. The latter condition results in slow step growth and simplifications in determining the conditions at the step boundaries, especially the step velocity. More recently interest has been directed towards adapting this earlier work to the conditions applicable to molecular-beam epitaxy (MBE) (Refs. 4–8) which lead to fast step growth and the possibility of different effects due to the growth and subsequent breakup of multiadatom islands on the terraces. For such situations the determination of the step velocity requires an additional consideration of the conditions prevailing at the step,[4–7] and the role of the boundary condition is especially significant. Regardless of the approach being used, the step-boundary condition is a necessary ingredient of the complete description, and the results will depend on how accurately this is specified.

Our purpose here is to reexamine the commonly used Chernov[9] radiation boundary condition (rbc) which replaces the equilibrium condition used in the pioneering work of Burton, Cabrera, and Frank[3] (BCF) for the case of CVD conditions. The motivation for this, beyond its own intrinsic interest, lies in subsequent use of the results obtained in the more complicated MBE case where, as noted earlier, the role of the boundary condition takes on an even greater importance and more recent work[4,6,8,10] has replaced the equilibrium condition used earlier[7,8] in this context with the rbc.

The approach we will use here is the microscopic formulation of the BCF theory used by us earlier[11,12] together with the equilibrium boundary condition. The level of approximation used here is chosen to be consistent with that of the BCF theory since our purpose is to obtain a clearer understanding at this level rather than a higher-order theory. The details regarding this formulation and the accompanying approximation procedure have been described by us elsewhere[11,12] and will not be repeated here. We begin in Sec. II with a consideration of the issues involved in specifying the boundary conditions at the steps for the case of CVD, which we consider here.

In Sec. III we obtain our primary goal of determining the precise form of the step boundary condition which is a modified rbc of the kind used for studying MBE;[6] we also obtain explicit results for the rate parameter in terms of the step-kicking coefficient. We conclude this paper in Sec. IV by considering the special case where the steps absorb all incident adatoms. Our formulation also allows us to determine the nonzero value of the adatom concentration at the step.[12]

In a macroscopic description such as the BCF model, the boundary condition is often a construct, based on intuition guided by judgment. The rbc appears to fall into this category in the present context. The point of what follows is not that this is incorrect, in fact we show that it can be made operationally correct, but rather that it is possible to input the identical microscopic information in a more compact and what we believe is a more transparent boundary condition that is consistent with the terrace-step exchange process.

II. RADIATION BOUNDARY CONDITION

While a variety of boundary conditions have been used together with the BCF kinetic description[3–6,9] most recent work has adopted the Cherenov rbc (Ref. 9)

$$|J(x=-\tfrac{1}{2}l)|=|j_{\rm in}(x=-\tfrac{1}{2}l)|-j_{\rm out}(x=-\tfrac{1}{2}l) \quad (1a)$$

$$=k[n(x=-\tfrac{1}{2}l)-n^0]\ , \quad (1b)$$

where we consider a step of length l centered at $x=0$ with symmetric kinetics at each end. The step exchange current $|J|$ is the difference between the incident and exit currents, n is the adatom concentration, n^0 is the equilibrium value of the latter quantity, and k is an input parameter describing the step kinetics.

For CVD the equilibrium condition is determined by a balance between the incident bulk vapor flux and the evaporating surface adatoms and the exchange current does not vanish—indeed, as noted earlier, BCF (Ref. 3) and others used an equilibrium step-boundary condition in their analysis. A consequence of Eq. (1b) then is that for

CVD conditions k must depend on the system parameters (e.g., the supersaturation and temperature) in a manner such that when the step density approaches its equilibrium value $k \to \infty$ so that $|J| =$ const, and likewise when the steps block, $J = 0$, $k \to 0$.[4] Thus, if Eq. (1b) were strictly correct k should command our interest relative to determining the functional dependence that leads to such limiting behavior. A previous justification of Eq. (1b) has been given but this is not self-contained and depends on an assumed step equilibrium condition.[4]

One final, relatively minor point worth mentioning here with regard to Eq. (1b) is that this equation is necessarily used with Fick's law relating current and concentration

$$J(x) = -Dn_x(x) \tag{1c}$$

with D the surface diffusivity. This result is suspect in general near a boundary, although not at the level of approximation we consider here, and in addition we will show that D must be modified to reflect the effect of evaporation in reducing the mean-square displacement.[11]

The microscopic formulation that we will use has been described elsewhere.[11,12] The particular advantage of this approach here is that it allows us to introduce a natural boundary condition in terms of an effective sticking coefficient, S, which describes the efficiency of the structureless step sink in capturing incident adatoms. If we denote incident (emergent) adatoms at the left step as n_2 (n_1) then

$$S = (n_2 - n_1)/n_2 \; . \tag{2}$$

Here $n_2(x)$ and $n_1(x)$ are concentrations of adatoms moving to the left and right on the terrace and, for simplification, any argument evaluated at the left step, $x = -\frac{1}{2}l$, will be omitted.

In the next section we use Eq. (2) as the boundary condition, i.e., S replaces k as the input parameter, and determine the exchange current in terms of n, n^0, S, and the remaining system parameters.

III. STEP-BOUNDARY CONDITION

The microscopic generalization[11,12] of the BFC kinetic equation allows us to identify concentrations and currents arising from particles moving left and right on the terrace. Thus, at the step we can specify incident and exit concentrations and currents in contradistinction to the macroscopic description which only provides the total values of these quantities. We will consider the case of symmetric step conditions, for which we have previously shown that the general solution to the microscopic kinetic equation is[11]

$$n(x) = \tfrac{1}{2}[n_1(x) + n_2(x)]$$

$$= n^0(1+\sigma) + 2A \cosh\lambda x \; , \tag{3a}$$

$$J(x) = (\alpha/2\pi)^{1/2}[n_1(x) - n_2(x)]$$

$$= -2A\frac{\lambda\alpha}{\zeta'}\sinh\lambda x \; , \tag{3b}$$

where σ is the supersaturation, $\alpha = k_B T/m$ with k_B Boltzmann's constant and m the adatom mass, A is a constant to be determined by the boundary condition, and $\lambda = (\zeta'/\alpha\tau)^{1/2}$ with $\zeta' = \zeta + \tau^{-1}$. The friction coefficient ζ is related to the diffusivity according to Einstein's relationship $\zeta = \alpha D^{-1}$ and τ is the desorption relaxation time for adatoms on the surface. Note that the length scale that occurs here is somewhat different than that appearing in the macroscopic description, $(D\tau)^{1/2}$, which does not account for desorption effects. The above results, which also indicate the separate contributions from left- and right-moving adatoms, are based on an approximate solution to the microscopic kinetic equation that is consistent with the classical BCF level of description. This can be systematically improved[11] if desired but this is not our interest here and will not be pursued.

The constant A in Eq. (3) is determined in terms of the quantity S defined in Eq. (2),

$$A = -Sn^0(1+\sigma)/2[(1-\tfrac{1}{2}S)(2\pi/\alpha)^{1/2}(\lambda\alpha/\zeta')\sinh\tfrac{1}{2}\lambda l + S\cosh\tfrac{1}{2}\lambda l] \; . \tag{4}$$

We can then use Eqs. (3) to determine the incident current, $|j_2| = n_2(\alpha/2\pi)^{1/2}$, and exit current, $j_1 = n_1(\alpha/2\pi)^{1/2}$, and we find

$$|j_2| = (2\alpha/\pi)^{1/2} n/(2-S) \equiv k_A n \; , \tag{5a}$$

$$j_1 = (1+\sigma)(1-S)(\lambda\alpha/\zeta)\sinh\tfrac{1}{2}\lambda l[S\cosh\tfrac{1}{2}\lambda l + (1-S)(\pi/2\alpha)^{1/2}(\lambda\alpha/\zeta')\sinh\tfrac{1}{2}\lambda l]^{-1} n^0$$

$$\equiv k_D n^0 \; . \tag{5b}$$

From Eq. (5b) we see that the necessary condition $j_1 = 0$ when $S = 1$ is satisfied, and from Eqs. (5) we see that for the blocking condition $S = 0$, $j_1 = |j_2|$ as required. Since $0 \le S \le 1$ and both hyperbolic functions are never negative it follows that neither k_A nor k_D can be infinite. Equations (5) are our primary results. They demonstrate that the natural boundary condition at the steps is not the rbc relating total current and driving force ($n - n^0$), as in Eq. (1b), but rather

$$|J| = k_A n - k_D n^0 \; . \tag{6}$$

If we write $k_D n^0 = k_{D'} n_s$ then Eq. (6) reduces to the form of the rbc that is sometimes used in place of Eq. (1b).[6]

The above results prescribe the general form of the step-boundary condition and also define the two rate parameters in terms of the step-sticking coefficient, which we now briefly consider.

Both k_A and k_D remain finite when $n=n^0$ and it is of some interest to consider the values these quantities take on for that case. The attachment coefficient k_A is already in an explicit form with the dependence on the sticking coefficient and temperature clearly evident. However, since n is also a function of these variables, k_A alone does not fully describe the dependence of j_2 on these quantities. Interestingly enough, k_A is independent of the supersaturation. The detachment coefficient, k_D, has a much more complicated structure, with functional dependence on all of the system parameters including the step length, l, and generalized friction coefficient ζ' as well as T, S, and σ. In the case of equilibrium we have from Eqs. (3a) and (4),

$$k_D=S^{-1}(1-S)\sigma\tanh\tfrac{1}{2}\lambda l\ ,\quad S>0\ . \tag{7}$$

In order for the blocking condition $S=0$ to occur at equilibrium the supersaturation σ must vanish, and for this special case we find that $k_D=k_A=(\alpha/2\pi)^{1/2}$.

We have shown that the rbc as specified by Eq. (1b) is not the natural boundary condition; however, for operational purposes this condition can be used. This form of the rbc can be extracted from our present formalism by evaluating the constant A in the general solution for $n(x)$, Eq. (3a), using the rbc and equating the result with that obtained above. In the former case

$$A'=-kn^0\sigma/[2k\cosh\tfrac{1}{2}\lambda l+(2\lambda\alpha/\zeta')\sinh\tfrac{1}{2}\lambda l] \tag{8}$$

and equating that to Eq. (4) we obtain

$$k=\frac{S(1+\sigma)(\lambda\alpha/\zeta')\sinh\frac{1}{2}\lambda l}{\sigma[(2-S)(\pi/2\alpha)^{1/2}(\lambda\alpha/\zeta')\sinh\frac{1}{2}\lambda l+S\cosh\frac{1}{2}\lambda l]-S(1+\sigma)\cosh\frac{1}{2}\lambda l}\ . \tag{9}$$

The origin of the required behavior of k at equilibrium can now be understood, since for this case we have from Eqs. (3) that the bracketed quantity in the denominator above is identically $S(1+\sigma)\sigma^{-1}\cosh\frac{1}{2}\lambda l$ so that $k\to\infty$. We can therefore conclude that the rbc, Eq. (1b), is equivalent to the more general, and we believe more transparent, form given by Eq. (6); Eqs. (5) and (9) then express the rate parameters in terms of the step-sticking coefficient.

IV. ABSORBING STEPS

Although it is most common in the macroscopic descriptions to use $n=0$ at the steps as the boundary condition describing absorbing steps,[5] from Eq. (6) it follows that when $k_D=0$, $n=0$ only when k_A becomes infinite. For finite k_A the step density remains finite; we can describe this case by setting $n_1(-\frac{1}{2}l)=n_2(\frac{1}{2}l)=0$, and from Eqs. (3) with this boundary condition we find

$$A=-n^0(1+\sigma)/[2\cosh\tfrac{1}{2}l\lambda+2A\sinh\tfrac{1}{2}l\lambda] \tag{10}$$

with $\lambda=(\xi'/\alpha\tau)^{1/2}$, $A=(\pi/2\xi'\tau)^{1/2}$, so that the step density $n_s=n(\pm l)$ is

$$n_s=n^0(1+\sigma)2A\sinh\tfrac{1}{2}l\lambda/[\cosh\tfrac{1}{2}l\lambda+\sinh\tfrac{1}{2}l\lambda] \tag{11}$$

and for $n_s=n^0$ we have the constraint

$$\coth\tfrac{1}{2}l\lambda=A(1+2\sigma)\ . \tag{12}$$

The above result could be made quantitatively more precise by utilizing a higher-order approximation,[11] however the conclusion that the conditions constraining the step equilibrium are derivable from the kinetic description is, we believe, worth further consideration.

In conclusion, we briefly consider the extension of the above results for the case of MBE conditions. This provides a relatively simple model for illustrating some of the differences between the different absorbing boundary conditions. In the step-flow regime, for which moving boundary, nucleation, and desorption effects can all be neglected,[3] the adatom concentration is described by

$$Dn_{xx}+F=0 \tag{13}$$

with F the beam source. For the usual macroscopic boundary condition, corresponding to $k_A\to\infty$, the concentration at the steps is zero, $n_M(\pm l)=0$, and for the microscopic boundary condition used above, corresponding to finite k_A we find, respectively,

$$n_M=(F/8D)(l^2-4x^2)\ , \tag{14a}$$

$$n=n_M+\tfrac{1}{2}Fl(\pi/2\alpha)^{1/2}=n_M+n_m\ . \tag{14b}$$

This result is quite different than that found for the case of a semi-infinite medium[13] where outside of a boundary layer the macroscopic solution remains valid. Here there is no boundary layer, however there is a microscopic correction term that persists across the terrace. To estimate the importance of this we can compare it to the midterrace value of the concentration found from Eq. (14b),

$$n_m/n_M|_{x=0}=(8\pi/\alpha)^{1/2}D/l\cong 2a/l\ , \tag{15}$$

where we have taken $D=a^2/2\tau$, $\alpha^{1/2}=(2\pi)^{1/2}a/\tau$, the average speed, and a is the site density. For GaAs, typical small-angle miscuts result in values of l/a in the range 10–25 and the effect we have described is small but not negligible. For Si, which has a slightly smaller lattice constant, the situation is very similar.

When the step velocity is taken into account the concentration profile becomes skewed and their values at the steps can only be equal if the step exchange kinetics are asymmetric. In this context the macroscopic absorbing boundary condition, $n(\pm l)=0$, is inconsistent as it implies both equal concentrations and symmetric attachment kinetics at the steps.

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