Homogenization of reconstructed crystal surfaces: Fick's law of diffusion

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(Received 22 January 2009; published 14 May 2009)

Fick's law for the diffusion of adsorbed atoms (adatoms) on crystal surfaces below roughening is generalized to account for surface reconstruction. In this case, material parameters vary spatially at the microscale, and the coarse graining for crystal steps via Taylor expansions is not strictly applicable. By invoking elements of the theory of *composites* in one independent space dimension, we homogenize the microscale description to derive the macroscopic adatom flux from step kinetics. This approach relies on a *multiscale expansion* for the adatom density. The *effective surface diffusivity* is determined through appropriate *discrete averages* of microscale kinetic parameters.

I. INTRODUCTION

Below the roughening transition, crystal surfaces slightly miscut with respect to a low-index orientation consist of nanoscale terraces separated by atomic line defects (steps) [1,2]. Stepped surfaces have long played a critical role in crystal growth, thin film epitaxy, surface chemistry and catalysis, yet their near-equilibrium properties remain the subject of intensive studies. A crucial issue is to understand how the *microscale* step kinetics influences surface morphologies at the *macroscale* [2].

Semiconductor surfaces exhibit distinct structural phases that depend on various conditions such as temperature and misorientation angle. This surface reconstruction (SR) has been the focus of theoretical and experimental works (see [3–6] for reviews). Hundreds of phases for Si have been reported [7]. For example, a type of SR on Si(100) is manifested by the formation on each terrace of dimer rows in one of two possible directions, parallel or perpendicular to step edges [8–11]. Material parameters, e.g., the terrace diffusivity, can then vary significantly across neighboring terraces. Despite such microscopic *inhomogeneities*, the surface appears *homogeneous* at large scales. Here, we derive a macroscopic law for the adatom flux *consistent* with the SR microstructure by properly averaging out microscale details.

The notion of averaging is central in the theory of composites [12,13]. Three *well-separated* scales are assumed: (i) the microscale, where inhomogeneities are evident; (ii) the *mesoscale*, where the system appears homogeneous and the analysis is carried out conveniently; and (iii) the macroscale. For the system of crystal steps, the microscale pertains to essentially one terrace, the mesoscale describes a sample of many steps, and the macroscale expresses a macroscopically large sample of the surface. The idea is to decouple the mesoscale and macroscale descriptions: in the latter, local averages of fields satisfy *homogenized* laws with *effective* material parameters.

In this Brief Report, we apply a version of homogenization theory [12,14,15] to extend Fick's macroscopic law of adatom diffusion, an ingredient of crystal surface evolution, to terraces characterized by a sequence of *distinctly different kinetic parameters* in one space dimension (1D). Generally, Fick's law has the form

$$\mathbf{J}_{av} = -\mathbf{D}_e(\boldsymbol{\nabla} h) \cdot \boldsymbol{\nabla}\rho_{av}, \quad \boldsymbol{\nabla} = (\partial_x, \partial_y), \tag{1}$$

where $\mathbf{J}_{av}$ and ρ_{av} are local averages of the adatom flux and density, and $\mathbf{D}_e$ is an effective diffusivity (a scalar coefficient in 1D). Previous macroscopic models for stepped surfaces invoke Eq. (1) by the assumption that microscale material parameters are constants across terraces and steps [16–22]. In that case, Eq. (1) is derived via standard coarse graining: discrete variables for consecutive steps are viewed as interpolations of smooth (continuous) functions and are Taylor expanded accordingly. This approach is deemed inadequate for SR. Here, we derive $\mathbf{D}_e$, and the related surface mobility, via *particular averages* of terrace diffusivities and step kinetic rates. We also discuss the extension of our results to two independent space dimensions (2D), where $\mathbf{D}_e$ is strictly a tensor [22].

Besides the scale separation outlined above, we postulate that steps are smooth boundaries (e.g., straight lines in 1D) and are subject to deterministic linear kinetics. These assumptions follow the celebrated Burton-Cabrera-Frank (BCF) model [1,23].

We start with the formalism for diffusion in layered media described by Holmes [14], who applies continuity of density *and* flux at the microscale. For mathematical convenience, we take the adatom flux to be continuous at each step edge. Thus, by mass conservation steps do not move. This assumption appears paradoxical in the context of surface evolution. In fact, it may be interpreted as an approximation for long times, as discussed in the conclusions. The adatom density here is allowed to have a *jump discontinuity* at every edge [see Eq. (2)]. This approach not only suffices to yield Fick's law, whose form and parameters are independent of the step velocity and energetics, but also aims to shed light on the nature of this law from a multiscale perspective. Determining the *evolution* of the surface height requires, in addition, the description of the (rather complicated in SR) step interactions. This aspect is not addressed in this Brief Report.

II. 1D MICROSCALE MODEL

The problem geometry is shown in Fig. 1. The step train is monotonic, with step positions $x_0, \ldots, x_N$ and atomic
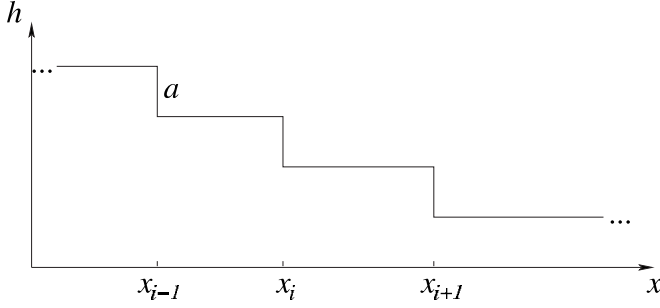
FIG. 1. Schematic of steps (side view): a is the step height. For straight steps (in 1D), $x=x_i$ at the ith step edge.

height a, where $0<x_i-x_{i-1}=\mathcal{O}(a)$ [24], $i=1,\ldots,N(N\gg1)$. At the ith step edge, we impose the kinetic conditions

$$f_i=k_i(\rho_i-\rho_i^{\text{eq}}), \quad -f_i=k_i(\rho_{i+1}-\rho_i^{\text{eq}}) \ (x=x_i), \quad (2)$$

where ρ_i^{eq} is the equilibrium adatom density [1] and $f_i=J_i(x_i)=-J_{i+1}(x_i)$ is the mass flux at the ith step edge with attachment-detachment kinetic rate k_i. Note that $\rho_i(x)$ and $J_i(x)=-D_i(x)\partial_x\rho_i$ are the adatom density and flux, respectively, on the ith terrace, i.e., the region $x_{i-1}<x<x_i$, and $D_i(x)$ denotes the corresponding terrace diffusivity. By Eq. (2), the adatom flux is continuous while the density has the jump $\rho_{i+1}-\rho_i=-(2/k)f_i$ at x_i. This $\rho_i(x)$ satisfies the steady-state diffusion equation, $\partial_x[D_i(x)\partial_x\rho_i]=0$, in the quasisteady approximation. Each $D_i(x)$ and k_i has lower and upper positive bounds (to be invoked later). In typical situations of SR, D_i and k_i may form periodic sequences. The step height, a, is a constant in our analysis. We will see that our major results are independent of this assumption (and can in fact include a's that vary with i). Rates k_i different for up- and down-step edges [25,26] can be incorporated directly, as is shown below.

The step train described above is viewed as a mesoscale constituent element, of size $d=\mathcal{O}(Na)$, of the large-scale surface morphology of size $\lambda(d\ll\lambda)$. We introduce the small (nondimensional) parameter $\epsilon=a/d=\mathcal{O}(1/N)$, where $(x_i-x_{i-1})/d=\mathcal{O}(\epsilon)$. Equation (1) will be derived in the limit $\epsilon\to0$ with $N\epsilon=\mathcal{O}(1)$ [22].

III. MULTISCALE EXPANSION

For $\epsilon\ll1$ the adatom flux and density depend on the macroscopic (slow) variable x *and* the microscopic (fast) variable $\tilde{x}=(x-\check{x})/\epsilon$ [12,14]. We choose $\check{x}=x_0$ so that $\tilde{x}_0\equiv\tilde{x}|_{x=x_0}=(x_0-\check{x})/\epsilon=0$ for later algebraic convenience. The density $\rho_i\equiv\rho$ is replaced (in an appropriate sense) by the *global* expansion

$$\rho=\rho^{(0)}(x,\tilde{x})+\epsilon\rho^{(1)}(x,\tilde{x})+\epsilon^2\rho^{(2)}(x,\tilde{x})+\cdots, \quad (3)$$

where $\rho^{(l)}$ are ϵ-independent, *bounded* coefficients (which should not be confused with derivatives of ρ). The operator ∂_x is thus replaced by $\epsilon^{-1}\partial_{\tilde{x}}+\partial_x$. Next, we substitute Eq. (3) into the diffusion equation for ρ_i and condition (2) at every point $\tilde{x}_i\equiv\tilde{x}|_{x=x_i}$. Naturally, we will separate terms sharing the same powers of ϵ to obtain and solve a *cascade* of equations

for $\rho^{(l)}$. In view of Eq. (3), the flux $J_i=J$ is expressed formally by [27]

$$J=-\epsilon^{-1}D_i(\partial_{\tilde{x}}+\epsilon\partial_x)[\rho^{(0)}+\epsilon\rho^{(1)}+\epsilon^2\rho^{(2)}+\cdots]. \quad (4)$$

The macroscopic limit of (ρ_i,J_i) is $(\rho^{(0)},J^{(0)})$, anticipated to be $\tilde{x}$ independent. As is typical in homogenization problems, fully determining this limit requires applying solvability conditions to higher-order terms $\rho^{(l)}$. [Expansion (3) is in essence a singular perturbation.]

IV. HOMOGENIZATION CASCADE AND MAIN RESULTS

By the balance of $\mathcal{O}(\epsilon^0)$ terms, $\rho^{(0)}$ satisfies $\partial_{\tilde{x}}[D_i(x)\partial_{\tilde{x}}\rho^{(0)}]=0$, by which $\rho^{(0)}=A_i(x)\tilde{x}+B_i(x)$, where $A_i,B_i=\mathcal{O}(1)$. Hence, by Eq. (4), $J=-\epsilon^{-1}D_iA_i+\mathcal{O}(1)$ and the continuity of flux at every point $\tilde{x}=\tilde{x}_i$ yields $D_iA_i=D_1A_1$. By Eq. (2) we apply the jump condition $\rho_{i+1}-\rho_i=-(2/k)A_i$ at $\tilde{x}_i$, which entails $B_{i+1}-B_i=(A_i-A_{i+1})\tilde{x}_i+dq_iA_i$ where $q_i\equiv2D_i/(k_ia)=\mathcal{O}(1)$ [22]. By summing up the differences $B_{i+1}-B_i$ we obtain $B_i(x)$ in terms of $A_1(x)$ and $B_1(x)$. Consequently, $\rho^{(0)}$ is found to be

$$\rho^{(0)}(x,\tilde{x})=\frac{D_1A_1}{D_i}(\tilde{x}-\tilde{x}_i)+B_1+A_1D_1\tilde{x}_i[\mathcal{S}_i(x)+\mathcal{Q}_i(x)],$$
$$\tilde{x}_{i-1}<\tilde{x}<\tilde{x}_i, \quad (5)$$

where the sums $\mathcal{S}_i(x)\equiv\tilde{x}_i^{-1}\Sigma_{j=1}^i(\tilde{x}_j-\tilde{x}_{j-1})/D_j(x)$ and $\mathcal{Q}_i(x)\equiv d\tilde{x}_i^{-1}\Sigma_{j=1}^{i-1}q_j/D_j(x)$ are bounded below and above (because so is each D_j and k_j) as $i\to\infty$. Indeed, by defining $D_{\text{m}}\equiv\min_i\{D_i\}$, $D_{\text{M}}\equiv\max_i\{D_i\}$, $k_{\text{m}}\equiv\min_i\{k_i\}$, $k_{\text{M}}\equiv\max_i\{k_i\}$, we have $D_{\text{M}}^{-1}\leq\mathcal{S}_i\leq D_{\text{m}}^{-1}$ and $m_i(q_{\text{m}}/D_{\text{M}})\leq\mathcal{Q}_i\leq m_i(q_{\text{M}}/D_{\text{m}})$, where $m_i\equiv(i-1)a/(x_i-x_0)=\mathcal{O}(1)$ and $q_{\text{m}}(q_{\text{M}})$ is the smallest (largest) value of q_i (suppressing the x dependence). As $i\to\infty(\tilde{x}_i\to\infty)$, $\rho^{(0)}$ must also be bounded. Thus, we set $A_1(x)\equiv0$ [14], which yields the leading-order term

$$\rho^{(0)}(x,\tilde{x})=B(x) \quad (\partial_{\tilde{x}}B\equiv0,B:=B_1). \quad (6)$$

In hindsight, this result is obtained if we require that the flux be $\mathcal{O}(1)$. By Eq. (4), $J=-\epsilon^{-1}D_1A_1(x)+\mathcal{O}(1)$. Thus, one may set $A_1\equiv0$ to eliminate the $\mathcal{O}(\epsilon^{-1})$ term.

To the next higher order, by collection of $\mathcal{O}(\epsilon)$ terms, $\rho^{(1)}$ satisfies $\partial_{\tilde{x}}[D_i\partial_{\tilde{x}}\rho^{(1)}]=0$, which is solved by $\rho^{(1)}(x,\tilde{x})=C_i(x)\tilde{x}+F_i(x)$ for $\tilde{x}_{i-1}<\tilde{x}<\tilde{x}_i$. By Eq. (4), $J=-D_i[C_i(x)+\partial_xB]+\mathcal{O}(\epsilon)$. Hence, the continuity of the adatom flux yields $C_i=(D_1/D_i)(C_1+\partial_xB)-\partial_xB$. The jump condition $\rho_{i+1}-\rho_i=-(2/k)J$ at $\tilde{x}_i$ yields the recursion formula $F_{i+1}-F_i=D_1(C_1+\partial_xB)[q_iD_i^{-1}d+(D_i^{-1}-D_{i+1}^{-1})\tilde{x}_i]$. By summing up these differences we obtain F_i in terms of C_1, F_1, and B. The resulting $\rho^{(1)}$ is

$$\rho^{(1)}=\left[\frac{D_1}{D_i}(C_1+\partial_xB)-\partial_xB\right](\tilde{x}-\tilde{x}_i)+F_1-\tilde{x}_i$$
$$\times\{\partial_xB-D_1(C_1+\partial_xB)[\mathcal{Q}_i(x)+\mathcal{S}_i(x)]\}, \quad (7)$$

where $\tilde{x}_{i-1}<\tilde{x}<\tilde{x}_i$, and $\mathcal{Q}_i(x)$ and $\mathcal{S}_i(x)$ are defined above. Since $\rho^{(1)}(x,\tilde{x})$ is required to be bounded as $i\to\infty$, we impose $\lim_{i\to\infty}\{\partial_xB-D_1(C_1+\partial_xB)[\mathcal{Q}_i(x)+\mathcal{S}_i(x)]\}=0$. This condition leads to the crucial relation

$$\mathcal{D}_{\mathrm{av}}\partial_x B = D_1(C_1 + \partial_x B)(1 + q_{\mathrm{av}}m^{(0)}), \qquad (8)$$

where $m^{(0)} \equiv d \lim_{i\to\infty}(i/\tilde{x}_i) = \lim_{i\to\infty}[ia/(x_i-x_0)] = \mathcal{O}(1)$. The (discrete) averages $\mathcal{D}_{\mathrm{av}}$ and q_{av} are defined by

$$\mathcal{D}_{\mathrm{av}}^{-1}(x) \equiv \lim_{i\to\infty}\mathcal{S}_i(x) = \lim_{i\to\infty}\left[\tilde{x}_i^{-1}\sum_{j=1}^{i}\frac{\tilde{x}_j - \tilde{x}_{j-1}}{D_j(x)}\right], \qquad (9)$$

$$q_{\mathrm{av}} = \frac{2\mathcal{D}_{\mathrm{av}}}{k_{\mathrm{av}}a} = \mathcal{O}(1), \quad k_{\mathrm{av}}^{-1} \equiv \lim_{i\to\infty}\left(\frac{1}{i}\sum_{j=1}^{i}\frac{1}{k_j}\right). \qquad (10)$$

A few remarks on Eqs. (8)–(10) are in order. First, bearing in mind that the calculation is carried out at the mesoscale, we identify $m^{(0)}$ with the local step density or positive surface slope, i.e., the macroscopic variable $m(x)=|\partial_x h|$ at $x_0 \approx x$ (slow coordinate). Second, formulas (8)–(10) remain valid in the case with a sequence of step heights, $\{a_i\}$. This becomes clear through defining the height change $ia(i) \equiv \Sigma_{j=1}^{i}a_j$. Then, it suffices to use the slope $m^{(0)} = \lim_{i\to\infty}[ia(i)/(x_i-x_0)]$, where $q_{\mathrm{av}} \equiv 2\mathcal{D}_{\mathrm{av}}/(k_{\mathrm{av}}a_{\mathrm{av}})$, $a_{\mathrm{av}} \equiv \lim_{i\to\infty}a(i)$. Generally, one can replace x_0 by $\check{x}$, where $x_{i^*-1} < \check{x} < x_{i^*}(1 < i^* < N)$: $m^{(0)}$ becomes $\lim_{i\to\infty}[|i -i^*|a(i)/(|x_i-\check{x}|)]$, the slope at $\check{x} \approx x$, where summations are carried out over $j \geq i^*$.

Third, Eqs. (8)–(10) form a nontrivial extension of the averaging carried out in [14] for diffusion in layered media. For comparison, define the effective diffusivity

$$\mathcal{D}_{\mathrm{e}}(x;m) \equiv \frac{\mathcal{D}_{\mathrm{av}}(x)}{1 + q_{\mathrm{av}}m(x)}. \qquad (11)$$

The corresponding parameter found in [14], where continuity of density is applied, ensues from Eq. (11) in the limit $q_{\mathrm{av}} \to 0$, or by taking $k_j \to \infty$ for all j, i.e., in the case of diffusion-limited kinetics. So, the appearance of $m=|\partial_x h|$ in Eq. (11) is the macroscopic signature of jump discontinuities of ρ at the microscale.

Lastly, suppose that an Ehrlich-Schwoebel barrier is present, so that the kinetic rate $(k_{i,\mathrm{u}})$ for an up-step edge is different from that $(k_{i,\mathrm{d}})$ for a down-step edge [25,26]. The jump discontinuity of ρ at $\tilde{x}_i$ is $(k_{i,\mathrm{d}}^{-1}+k_{i,\mathrm{u}}^{-1})J$. Thus, the k_j^{-1} term in Eq. (10) is replaced by $(k_{j,\mathrm{u}}^{-1}+k_{j,\mathrm{d}}^{-1})/2$.

It remains to express the adatom flux $J(x)$ in terms of $B(x)$ by virtue of condition (8). By Eq. (4), we have [27]

$$J = -D_1(C_1 + \partial_x B) = -\mathcal{D}_{\mathrm{e}}(x;|\partial_x h|)\partial_x B, \quad \epsilon \to 0. \quad (12)$$

This is Fick's law, Eq. (1), with $\mathbf{D}_{\mathrm{e}}=\mathcal{D}_{\mathrm{e}}\mathbf{1}$, $\mathbf{J}_{\mathrm{av}}=J(x)\mathbf{e}_x$, and $B(x)=\rho_{\mathrm{av}}(x)$ ($\mathbf{e}_x$: x-directed unit vector).

The consideration of the next higher-order term, i.e., the coefficient $\rho^{(2)}$ (and the respective flux), yields the condition $\partial_x(\mathcal{D}_{\mathrm{e}}\partial_x B)=0$. This equation is consistent with the mass conservation law $\partial_t h+\Omega\partial_x J=0$ (Ω: atomic area) if $\partial_t h \equiv 0$ (i.e., when steps do not move). Consider the tempting assumption (in lieu of a derivation) that $\rho_{\mathrm{av}}(x)$ is identified with the average equilibrium density $\rho^{\mathrm{eq}}(x)$, the continuum limit of ρ_i^{eq} in Eq. (2) (see, e.g., [28] for constant kinetic parameters). Note that $\rho_i^{\mathrm{eq}}=\rho_{*,i}\exp[\mu_i/(k_BT)] \approx \rho_{*,i}[1+\mu_i/(k_BT)]$, where μ_i is the step chemical potential and k_BT is the Boltzmann energy [1]. The nature of this ρ_{av} needs to be explored.

V. EXAMPLE

Now consider the special case where D_i and k_i take two possible values, i.e., $D_i=D_1,D_2$ and $k_i=k_1,k_2$, a situation analogous to that in *biphasic* systems [14]. Thus, we obtain $\mathcal{D}_{\mathrm{av}}=(\alpha_1 D_1^{-1}+\alpha_2 D_2^{-1})^{-1}$ and $k_{\mathrm{av}}=(\alpha_1' k_1^{-1}+\alpha_2' k_2^{-1})^{-1}$, where $\alpha_n=d_n/d$ and $\alpha_n'=N_n/N$, d_n is the total length occupied by D_n, and N_n is the total number of step edges having rate $k_n(n=1,2)$. This result is relevant to the "two region" model by Zhao, Weeks and Kandel [29] (see also [30]).

Next, we discuss possible extensions and limitations of our results, pointing to open questions. Issues of interest include *curved* steps (in 2D) and the assumption of zero step velocity used in our derivation of Fick's law.

VI. DISCUSSION

A. 2D case

We consider kinetic parameters $D_i=D_i(\mathbf{r})$ ($\mathbf{r}$: position vector) and k_i. The vector adatom flux $\mathbf{J}_i$ has now components both normal ($J_{i,\perp}$) and parallel ($J_{i,\parallel}$) to step edges. The step configuration can be described by the orthogonal coordinate system (η,σ), where $\eta=\eta_i$ specifies each step and σ gives the position along the step edge [22,28]. The kinetic boundary conditions (2) hold with $f_i=J_\perp(\eta_i,\sigma)$ being the flux component *normal* to the step edge at $\eta=\eta_i$. The jump discontinuity of the density *in* η is proportional to this transverse flux. On each terrace, the normal and longitudinal flux components are coupled through $\boldsymbol{\nabla}\cdot\mathbf{J}_i=0$.

The above homogenization results involving x in 1D should be appropriately extended to 2D. The density ρ now has the jump $-(2/k_i)J_{i,\perp}$ at $\tilde{\eta}_i=(\eta_i-\eta_0)/\epsilon$. The macroscopic *vector* flux $\mathbf{J}$ should be a generalization of Eq. (12). The normal flux component is expected to be

$$J_\perp = -\mathcal{D}_{\mathrm{e}}(\mathbf{r};|\boldsymbol{\nabla}h|)[\partial_\perp B(\mathbf{r})], \qquad (13)$$

where $\mathcal{D}_{\mathrm{e}}$ is defined by Eq. (11), m is replaced by $|\boldsymbol{\nabla}h|$, and $\tilde{x}$ is replaced by $\tilde{\eta}=(\eta-\eta_0)/\epsilon$ times a slowly varying metric coefficient that has the dimension of length [22]. By analogy with the case $D_i=D_{\mathrm{s}}=\mathrm{const}$ [22], it is plausible that the longitudinal flux component $J_\parallel$ has a slope-independent effective diffusivity [22],

$$J_\parallel = -\check{\mathcal{D}}_{\mathrm{av}}\partial_\parallel B(\mathbf{r}), \qquad (14)$$

where $\check{\mathcal{D}}_{\mathrm{av}}$ is a suitable homogenized coefficient. By speculation, $\check{\mathcal{D}}_{\mathrm{av}}=\mathcal{D}_{\mathrm{av}}$. Equations (13) and (14) are combined to give law (1) with

$$\mathbf{D}_{\mathrm{e}} = \mathcal{D}_{\mathrm{av}}\begin{pmatrix}(1 + q_{\mathrm{av}}|\boldsymbol{\nabla}h|)^{-1} & 0 \\ 0 & 1\end{pmatrix}, \qquad (15)$$

which is the representation of the diffusivity tensor in the (η,σ) coordinates ($\rho_{\mathrm{av}} \equiv B$). The detailed study of the 2D case, especially the effect of *terrace anisotropies* (which are common in SR), is left for future work.

B. Hypothesis of zero step velocity

In our preceding discussions, the adatom flux is considered as continuous across step edges. This assumption (tech-

nically speaking) relates Fick's law directly to microscale boundary conditions (2), independently of the step velocity, as in the case with constant kinetic parameters [22]. However, it remains to be argued that our hypothesis does not contradict the use of Fick's law within surface evolution. A plausible argument in 1D is provided by an attempt to include moving steps (thus step velocities) in homogenization. Then, by mass conservation the adatom flux has the jump $J_{i+1} - J_i = -(a/\Omega)v_i \approx -\epsilon^{-1}v_i d$ at $\tilde{x}_i$, where $v_i = \epsilon(d\tilde{x}_i/dt)$ is the ith-step velocity ($\Omega \approx a^2$). It is realized that incorporation of this condition in the above multiscale framework calls for *separating time scales* as well. For our purposes, steps move slowly. Take $\tilde{t} \equiv \epsilon^{\alpha}t = \mathcal{O}(1)$ where $\alpha > 0$ [so, $t = \mathcal{O}(\epsilon^{-\alpha}) \to \infty$], which is compatible with (yet not derivable from) the usual quasisteady approach to adatom diffusion [1]. The dominant balance in powers of ϵ for the fluxes stemming from $\rho^{(0)}$, $\rho^{(1)}$ does not capture the nonzero velocity: $v_i = \epsilon^{1+\alpha}d\tilde{x}_i/d\tilde{t}$ where $d\tilde{x}_i/d\tilde{t} \le \mathcal{O}(1)$, and thus $J_{i+1} - J_i \le \mathcal{O}(\epsilon^{\alpha})$ which yields continuous fluxes (zero jumps for J_i's) to the first 2 orders of the multiscale expansion. A rigorous argument regarding time scales is deemed necessary but lies beyond our present scope.

VII. CONCLUSION

Fick's law for the diffusion of adatoms in surface reconstruction was derived systematically via the homogenization of a BCF-type model in 1D. The effective surface diffusivity and adatom mobility involve discrete averages of microscale material parameters. The mathematical procedure applied here, based on multiscale expansions under singular perturbation, differs from the direct coarse graining of kinetic boundary conditions for steps applied previously to constant microscale parameters. An extension of the results to 2D was discussed but not carried out explicitly.

To firmly connect the macroscopic theory to experimental situations of reconstructed crystal surfaces, it is desirable to consider (i) terrace anisotropies (e.g., for Si and GaAs reconstructed surfaces [31]) and (ii) appropriate *statistical ensembles* of step configurations. In case (ii), the main parameters D_i and k_i must be viewed as functions of the microstructure realization in the particular ensemble under consideration. The study of the homogenized fields as limits of ensemble averages is a viable direction of near-future research.

[1] H.-C. Jeong and E. D. Williams, Surf. Sci. Rep. **34**, 171 (1999).

[2] J. W. Evans, P. A. Thiel, and M. C. Bartelt, Surf. Sci. Rep. **61**, 1 (2006).

[3] J. A. Venables, *Introduction to Surface and Thin Film Processes* (Cambridge University Press, Cambridge, UK, 2000).

[4] C. B. Duke, Chem. Rev. **96**, 1237 (1996).

[5] G. P. Srivastava, Rep. Prog. Phys. **60**, 561 (1997).

[6] W. Mönch, *Semiconductor Surfaces and Interfaces* (Springer, Berlin, 1995).

[7] V. G. Lifshits, A. A. Saranin, and A. V. Zotov, *Surface Phases on Silicon: Preparation, Structures and Properties* (Wiley, New York, 1994).

[8] D. J. Chadi, Phys. Rev. Lett. **43**, 43 (1979).

[9] R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. B **34**, 5343 (1986).

[10] O. L. Alerhand, A. N. Berker, J. D. Joannopoulos, D. Vanderbilt, R. J. Hamers, and J. E. Demuth, Phys. Rev. Lett. **64**, 2406 (1990).

[11] B. S. Swartzentruber, N. Kitamura, M. G. Lagally, and M. B. Webb, Phys. Rev. B **47**, 13432 (1993).

[12] G. W. Milton, *The Theory of Composites* (Cambridge University Press, Cambridge, UK, 2002).

[13] S. Nemat-Nasser and M. Hori, *Micromechanics: Overall Properties of Heterogeneous Materials* (Elsevier, Amsterdam, 1999).

[14] M. H. Holmes, *Introduction to Perturbation Methods* (Springer, New York, 1995), pp. 232, 233.

[15] G. A. Pavliotis and A. M. Stuart, *Multiscale Methods: Averaging and Homogenization* (Springer, New York, 2007).

[16] P. Nozières, J. Phys. (France) **48**, 1605 (1987).

[17] A. Rettori and J. Villain, J. Phys. (France) **49**, 257 (1988).

[18] M. Ozdemir and A. Zangwill, Phys. Rev. B **42**, 5013 (1990).

[19] H. Spohn, J. Phys. (France) **3**, 69 (1993).

[20] W. E. and N. K. Yip, J. Stat. Phys. **104**, 221 (2001).

[21] V. B. Shenoy and L. B. Freund, J. Mech. Phys. Solids **50**, 1817 (2002).

[22] D. Margetis and R. V. Kohn, Multiscale Model. Simul. **5**, 729 (2006).

[23] W. K. Burton, N. Cabrera, and F. C. Frank, Philos. Trans. R. Soc. London, Ser. A **243**, 299 (1951).

[24] By $f = \mathcal{O}(g)$ we mean that f/g is bounded as $a \to 0$.

[25] G. Ehrlich and F. Hudda, J. Chem. Phys. **44**, 1039 (1966).

[26] R. L. Schwoebel and E. J. Shipsey, J. Appl. Phys. **37**, 3682 (1966).

[27] This expression is interpreted in the weak sense [12].

[28] J. Quah, J. Young, and D. Margetis, Phys. Rev. E **78**, 042602 (2008).

[29] T. Zhao, J. D. Weeks, and D. Kandel, Phys. Rev. B **70**, 161303(R) (2004).

[30] J. Quah and D. Margetis (unpublished).

[31] R. J. Phaneuf (private communication).