

Phase field model for composite stepped surface

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We present a phase field model for the evolution of stepped surfaces with *distinct* material parameters across nanoscale terraces in surface diffusion. The model aims to capture the Burton-Cabrera-Frank (BCF)-type theory for the motion of *decorated* non-interacting steps separating composite terraces. Our work forms an extension of the phase field model by Hu et al. [Physica D **241**, 77 (2012)]. The transport processes are diffusion of adsorbed atoms (adatoms) on terraces and along step edges, and attachment-detachment of atoms at steps, enriched with sequences of distinct kinetic rates. Material deposition from above, desorption and Ehrlich-Schwoebel barriers are included. We discuss how the phase field model reduces to the (sharp-interface) BCF-type theory.

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I. INTRODUCTION

For the development of novel materials, it is desirable to control properties of crystal surfaces at small scales. A means of altering and possibly controlling crystal surface dynamics is to deposit solutes, e.g., CO coverages [1] and chains of C₆₀ [2], on the surface from above. This results in a “composite surface”, and can dramatically influence the shapes and stability of nanostructures.

Below the roughening transition, the crystal surface morphological evolution is driven by the motion of line defects (steps) of atomic size, a , according to the Burton-Cabrera-Frank (BCF) model [3, 4]. Linking step kinetics to large-scale surface evolution helps understanding how microscale details can be engineered to achieve appealing surface morphologies. This connection is largely unexplored for composite stepped surfaces. A partial differential equation (PDE) for the relaxation of the large-scale height profile was formally derived for composite surfaces in one spatial dimension (1D) [5]. However, a systematic, general macroscopic theory is still elusive.

In this Brief Report, we present a phase field model for a composite surface with non-interacting steps in two spatial dimensions (2D). The diffusion of adsorbed atoms (adatoms) on terraces and attachment/detachment of atoms at steps, which are key processes of the BCF theory [3], have kinetic rates that *vary* across terraces. Ehrlich-Schwoebel (ES) barriers [6], step edge diffusion, desorption and material deposition from above are included. We view the phase field as an initial yet requisite stage of developing a fully macroscopic theory. Our work was inspired by and is an extension of [7]; see also [8–10].

Our motivation is twofold. First, it is known that phase field models, which replace each step edge by a diffuse (boundary) layer of finite small width, are computationally appealing [11]; their use circumvents the need for explicitly tracking steps (free sharp boundaries in BCF theory). Second, microscale variables of interest such as the adatom density and flux, which can have jumps at step edges within BCF-type theories, become continuous

across boundary layers in the phase field model; hence, the passage to the full macroscopic limit, when the step height tends to zero, may become more amenable to systematic theory. For example, a difficulty in the rigorous study of the homogenized limit of a composite surface stems from the discontinuity of the microscale adatom density across step edges [5]. At the macroscale, the surface appears smooth, with a continuous adatom density.

The full macroscopic theory of decorated surfaces should incorporate some notion of *averaging* over *distinct* material parameters [5]. Determining such averages in 2D is an open problem. We do not address this issue here, but expect that the phase field model can be explored for further analytical insights into averaging.

Another appeal of the phase field model is that it contains features of both scales (nanoscale and macroscale). Indeed, the phase field gives rise to a continuum theory since step edges are smoothed out. At the same time, the boundary layer width, ϵ , controls the influence of boundary conditions at steps. Recovering the sharp-interface limit (BCF-type model) requires $\epsilon \rightarrow 0$. The full continuum limit results from $a \rightarrow 0$ with fixed slope.

A limitation of our model, as in [7], is its lack of step-step interactions. Step line tension, included in the formulation, is more important in only a limited number of cases, as we outline below. The incorporation of elastic-dipole interactions is the subject of work in progress.

The remainder of this Brief Report is organized as follows. Section II revisits elements of the BCF theory, and provides the equations of motion for steps. In Sec. III, we formulate the phase field model in the spirit of [7]. In Sec. IV, we argue that the phase field model yields the BCF-type theory. Lastly, Sec. V summarizes our results.

II. ELEMENTS OF BCF-TYPE THEORY

We start with elements of step motion [3]. The kinetic processes are: (i) diffusion of adatoms on terraces and step edges; (ii) attachment and detachment of atoms at

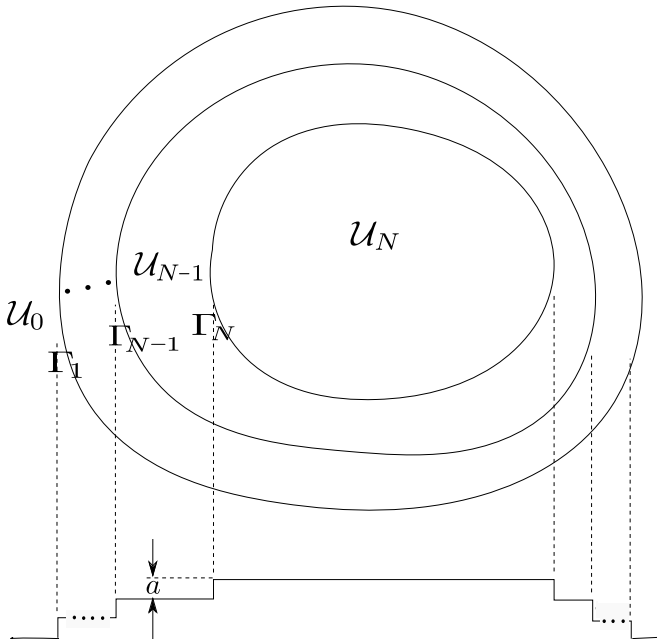


FIG. 1: Top and side views of steps and terraces in 2D. The symbol \mathcal{U}_i denotes the i th terrace, and Γ_i denotes the i th step edge ($i = 0, \dots, N$). The step height is a constant, a .

steps; (iii) desorption; and (iv) material deposition from above. Our model uses distinct diffusivities (on terraces and step edges) and sticking rates for atoms at steps.

First, we outline the step geometry. Consider N monolayers (or ordered steps); see Fig. 1. Let \mathcal{U}_i and Γ_i denote the i th terrace and step edge, respectively, where each Γ_i is smooth and non-self-intersecting; $i = 1, \dots, N$, $N \gg 1$, and Γ_0 lies far away (at infinity).

Adatom diffusion is characterized by (positive) diffusivity D_i in \mathcal{U}_i ; in addition, atoms attach/detach with kinetic rates k_i^\pm at Γ_i from the upper (+) or lower (-) terrace; see Eqs. (1). A system of such terrace-dependent diffusivities is the reconstructed Si(111) which may exhibit two phases simultaneously, with two values of D_i periodically alternating from one terrace to the next [12].

Now define $C_i = C_i(x, y, t)$ and $\mathbf{J}_i = -D_i \nabla C_i$ as the adatom density and flux on the i th terrace of the (x, y) -plane (basal plane). The adatom concentration satisfies the diffusion equation, $\partial_t C_i + \nabla \cdot \mathbf{J}_i = \mathcal{F} - \tau^{-1} C_i$ in \mathcal{U}_i , where \mathcal{F} is the deposition flux and τ is the desorption time. We employ the quasi-steady approximation, $\partial_t C_i \simeq 0$, by which $\nabla \cdot \mathbf{J}_i = \mathcal{F} - \tau^{-1} C_i$. Further, we apply linear kinetics for atom attachment/detachment at steps:

$$\mathbf{J}_i \cdot \mathbf{n}_i = k_i^+ (C_i - C_i^{\text{eq}}) \quad \text{on } \Gamma_i, \quad (1a)$$

$$-\mathbf{J}_{i-1} \cdot \mathbf{n}_i = k_i^- (C_i - C_i^{\text{eq}}) \quad \text{on } \Gamma_i, \quad (1b)$$

where \mathbf{n}_i is the unit vector normal to Γ_i pointing outward from \mathcal{U}_i , and k_i^+ (k_i^-) is the adatom attachment-detachment rate from the upper (lower) terrace at the i th step edge. With a positive ES barrier [6], adatoms

are more inclined to attach to a step edge from the lower terrace; thus, $k_i^+ < k_i^-$. If steps do not interact, the equilibrium concentration, C_i^{eq} , is given by [4]

$$C_i^{\text{eq}} \simeq C_* (1 + \sigma \kappa_i), \quad (2)$$

where C_* and σ are constants and κ_i is the (local) curvature of Γ_i ; $\sigma = \gamma/(k_B T)$, γ is the step stiffness, and $k_B T$ is the Boltzmann energy (absolute temperature).

A few remarks on step-step interactions, which we omit from our formulation, are in order. Steps may repel each other entropically and as elastic dipoles [4]. These interactions modify Eq. (2) to $C_i^{\text{eq}} \simeq C_* (1 + \sigma \kappa_i + e_i)$, where e_i has tractable forms for relatively simple step geometries in 2D [13]. For example, in the radial geometry (with concentric circular steps), e_i contains a term of the form $\psi(r_i, r_{i+1}) - \psi(r_{i-1}, r_i)$ where r_i denote the step radii, and $\psi(r_i, r_j)$ behaves as $|r_i - r_j|^{-3}$ [13, 14]. In other geometries in 2D, e_i has a complicated dependence on the coordinates [13]. Thus far, we have been unable to formulate a phase field model in correspondence to e_i ; this task is left for future work. The error caused by this deficiency of our model is expected to decrease with the linear size of each step, and be negligible when the step stiffness (curvature) tends to dominate over e_i .

The diffusion equation for C_i along with Eqs. (1) and (2) are complemented with the step velocity law, $v_i = (\Omega/a)(\mathbf{J}_i - \mathbf{J}_{i-1}) \cdot \mathbf{n}_i + a \partial_{s_i} (\nu_i \partial_{s_i} \kappa_i)$ on Γ_i , where v_i is the normal velocity of the i th step edge, ν_i is proportional to the step-edge diffusion coefficient, $\Omega \simeq a^3$ is the atomic volume, and ∂_{s_i} is the step-edge (arc-length) partial derivative. Finally, we assume that $\Gamma_0 \equiv \Gamma_\infty$ is a large circle of radius R_∞ ; one may think of R_∞ as a typical macroscopic length. By employing a uniform far-field condition [7], we require that $\frac{1}{2\pi} \int_{\Gamma_0} \mathbf{J}_0 \cdot \mathbf{n}_0 dS = J_\infty$, where we set $J_\infty = 0$ for algebraic convenience.

Next, we non-dimensionalize time and spatial variables via $t_* = R_\infty^2/D$ and $\ell_* = R_\infty$; D is a reference value for the diffusivities, say, $D = D_0$. We set $\tilde{t} = t/t_*$ and $(\tilde{x}, \tilde{y}) = (x/\ell_*, y/\ell_*)$, $\tilde{a} = a/\ell_*$. Define the non-dimensional concentration and flux: $\varrho_i = R_\infty^2 (C_i - C_*)$ and $\mathcal{J}_i = -\mathcal{D}_i \tilde{\nabla} \varrho_i$, where $\mathcal{D}_i = D_i/D$ and $\tilde{\nabla} = (\partial_{\tilde{x}}, \partial_{\tilde{y}})$. The adatom diffusion equation and step velocity law read

$$\tilde{\nabla} \cdot \mathcal{J}_i = \Lambda - \varsigma^2 (\varrho_i + \varrho_*) \quad \text{in } \mathcal{U}_i, \quad (3)$$

$$\tilde{v}_i \tilde{a}^{-2} = (\mathcal{J}_i - \mathcal{J}_{i-1}) \cdot \mathbf{n}_i + \tilde{a}^{-1} \tilde{\partial}_{s_i} (\beta_i \tilde{\partial}_{s_i} \tilde{\kappa}_i) \quad \text{on } \Gamma_i, \quad (4)$$

where the tildes on top of variables refer to the scaled-coordinate system. The kinetic boundary conditions read

$$\xi_i^+ \mathcal{J}_i \cdot \mathbf{n}_i = \varrho_i - \varrho_* \delta \tilde{\kappa}_i \quad \text{on } \Gamma_i, \quad (5a)$$

$$-\xi_i^- \mathcal{J}_{i-1} \cdot \mathbf{n}_i = \varrho_{i-1} - \varrho_* \delta \tilde{\kappa}_i \quad \text{on } \Gamma_i. \quad (5b)$$

In the above, $\tilde{v}_i = (R_\infty/D)v_i$, $\Lambda = \mathcal{F} R_\infty^4/D$, $\varsigma = R_\infty/\sqrt{D\tau}$, $\xi_i^\pm = D/(k_i^\pm R_\infty)$, $\delta = \sigma/R_\infty$, $\tilde{\kappa}_i = R_\infty \kappa_i$, $\varrho_* = C_* R_\infty^2$, and $\beta_i = \nu_i/(R_\infty D)$. For ease of notation, we drop the tildes from now on.

III. PHASE FIELD MODEL

We now focus on the phase field variable (order parameter) $\phi^\epsilon(x, y, t)$, a smooth approximation for the (discrete) height of the step configuration [7]; $\phi^\epsilon = ia$ on the i th terrace. Our goal is to replace the BCF-type model of Eqs. (3)-(5) by evolution laws involving ϕ^ϵ . These laws account for: (i) the rapid change of ϕ^ϵ across boundary layers (narrow regions near steps); and (ii) the condition that ϕ^ϵ approaches its appropriate constant value on each terrace away from steps. These two distinct behaviors are matched to produce a solution everywhere.

A complication of our model absent from [7] is the existence of the *sequences* $\{\xi_i^\pm, \mathcal{D}_i, \beta_i\}$. This feature is reflected into the *definition of coefficients in the laws for* ϕ^ϵ .

Equation (3) is replaced by the evolution law

$$a^{-2} [a^{-1} \partial_t \phi^\epsilon - \nabla_s \cdot (\beta \nabla_s \kappa) |\nabla \phi^\epsilon|] = \nabla \cdot [M(\phi^\epsilon; \epsilon) \nabla \varrho^\epsilon] + \Lambda - \varsigma^2 (\varrho^\epsilon + \varrho_*), \quad (6)$$

where $\varrho^\epsilon(x, y, t)$, defined continuously everywhere, is a (non-dimensional) field variable that smoothly approximates the adatom density; and $\kappa = \nabla \cdot \mathbf{n}$ and $\mathbf{n} = -\nabla \phi^\epsilon / |\nabla \phi^\epsilon|$ define the local curvature and normal vector everywhere. Also, $\nabla_s = (\mathbf{I} - \mathbf{nn}) \nabla$ is the gradient along curves of step edges, or height level sets (\mathbf{I} : unit tensor). Step velocity law (4) and conditions (5) are replaced by an additional equation of motion, viz.,

$$\alpha a^{-2} \epsilon^2 [a^{-1} \partial_t \phi^\epsilon - \nabla_s \cdot (\beta \nabla_s \kappa) |\nabla \phi^\epsilon|] = \epsilon^2 \Delta \phi^\epsilon - G'(\phi^\epsilon) + \frac{\epsilon}{\varrho_* \delta} \varrho^\epsilon, \quad (7)$$

where the prime denotes differentiation with respect to the argument. The coefficients of Eqs. (6) and (7) are defined below. These equations are supplemented with the boundary conditions that the normal derivatives of ϕ^ϵ and ϱ^ϵ vanish at Γ_∞ . Unlike the description in [9], Eqs. (6) and (7) do not contain a time derivative of ϱ^ϵ because of the quasi-steady approach. In the limit $\epsilon \rightarrow 0$, Eq. (6) reduces to Eq. (3) on each terrace; and both Eqs. (6) and (7) contribute to Eqs (4) and (5) at steps.

We now comment on the coefficients entering Eqs. (6) and (7). *The continuous mobility* M accounts for *distinct inhomogeneities due to* ξ_i^\pm and \mathcal{D}_i : $M(\phi; \epsilon) = \mathfrak{M}(1 + \epsilon^{-1} \zeta(\phi))^{-1}$. Here, \mathfrak{M} is a smooth function that yields terrace (i)-dependent diffusivities; more precisely,

$$\mathfrak{M}(\phi) = \eta_{a/4}(\phi) * \left[\sum_i \mathcal{D}_i \chi_{[(i-1/2)a, (i+1/2)a]}(\phi) \right]$$

where $\eta_{a/4}(y) = \frac{4}{a} \eta(\frac{4y}{a})$ is a mollifier with, e.g., $\eta(x) = C \exp[1/(|x|^2 - 1)]$ if $|x| < 1$ and 0 if $|x| \geq 1$; the $*$ operation denotes convolution; $\chi_S(\phi) = 1$ if ϕ lies in set S and 0 otherwise; and $C > 0$ is a constant such that $\int_{-\infty}^{\infty} \eta(x) dx = 1$. Step-dependent sticking rates are

included in $\zeta(\phi)$ defined by $\zeta(\phi) = \gamma_i [\phi - (i-1)a]^{p_i} (ia - \phi)^{q_i} G(\phi)$ for $\phi \in [(i-1)a, ia)$, where γ_i, p_i , and q_i satisfy

$$\alpha = \frac{1}{\varrho_* \delta} \int_0^a \frac{\zeta(\phi + (i-1)a)}{\mathfrak{M}(\phi + (i-1)a) \sqrt{2G(\phi)}} \phi(a - \phi) d\phi, \quad (8)$$

$$\xi_i^- = \int_0^a \frac{\zeta(\phi + (i-1)a)}{\mathfrak{M}(\phi + (i-1)a) \sqrt{2G(\phi)}} (a - \phi) d\phi, \quad (9)$$

$$\xi_i^+ = \int_0^a \frac{\zeta(\phi + (i-1)a)}{\mathfrak{M}(\phi + (i-1)a) \sqrt{2G(\phi)}} \phi d\phi. \quad (10)$$

The function $G(\phi)$ is the periodic multi-well free energy $G(\phi) = b[e^{f_i(\phi)} - 1][e^{f_{i+1}(\phi)} - 1]$ for $\phi \in [ia, (i+1)a)$ [7, 9]; $f_i(\phi) = c_1(ia - \phi)^2 + c_2(ia - \phi)^4$ where c_1 and c_2 are constants chosen conveniently for applications, e.g., $c_1 = 4.5$ and $c_2 = 0.9$ in [7]. Note that G changes rapidly away from step edges and indicates the position of terraces as a function of the height profile. The constant b is determined through $\int_0^a \sqrt{2G(\phi)} d\phi = 1$.

Furthermore, in Eqs. (6) and (7) we invoke the continuous function $\beta(\phi; \epsilon) = \sum_i (\beta_i - \beta_{i-1}) \left\{ 1 + e^{-\frac{[\phi - (i-1)a]}{\epsilon \ell}} \right\}^{-1}$ which accounts for step edge diffusion, with $\beta_0 \equiv 0$. The constant ℓ is positive, $\ell > 0$, and determines how fast β converges to the discontinuous function $\hat{\beta}(\phi) \equiv \sum_{i=1}^N \beta_i \chi_{[(i-1)a, ia]}(\phi)$; for all practical purposes, $\ell = 1$.

Our definition of the mobility function, $M(\phi; \epsilon)$, differs from the corresponding formulation in [7] where $\mathfrak{M}(\phi)$ is unity and the coefficients of $\zeta(\phi)$ do not depend on i . In particular, our $M(\phi; \epsilon)$ is non-periodic so that it can accommodate distinct diffusivities whereas it is periodic in [7]. Note that $\mathfrak{M}(\phi) \equiv \mathcal{D}_i$ if ϕ lies in $((i - \frac{1}{4})a, (i + \frac{1}{4})a)$. In Sec. IV, we show how this property of \mathfrak{M} leads to the terrace-dependent diffusion equations (3). Also, we introduce i -dependent parameters p_i, γ_i and q_i in $\zeta(\phi)$ to compensate for the i -dependence of ξ_i^\pm and the lack of periodicity of $M(\phi)$. Physically, ζ yields the requisite asymmetry of the ES barrier.

In view of the above, the BCF-type limit is described via ϕ^ϵ as follows. By defining $\Gamma_i(t; \epsilon)$ so that $\phi^\epsilon(x, y, t) = (i - 1/2)a$ for (x, y) in $\Gamma_i(t; \epsilon)$, the sharp interface stems from the limit $\Gamma_i(t; 0) \equiv \Gamma_i$ of $\Gamma_i(t; \epsilon)$ as $\epsilon \rightarrow 0$.

IV. OUTLINE OF MATCHING

Next, following [7] we formally discuss how the phase field model yields the BCF-type model for composite surfaces. The idea is to separate the spatial coordinate normal to each step into fast (z_i) and slow (r_i) variables via inner regions (boundary layers), in which the variation of ϕ^ϵ over z_i prevails; and outer regions where the slow variable is important [15]. A global solution for ϕ^ϵ is obtained by matching across each overlap region.

To describe ϕ^ϵ near the i th step, consider the orthogonal curvilinear coordinate system (r_i, s_i) near $\Gamma_i(t; \epsilon)$; $r_i = r_i^\epsilon(x, y, t)$ is the signed distance of (x, y) from $\Gamma_i(t; \epsilon)$ where $r_i > 0$ in the direction of \mathcal{U}_{i-1} , and $s_i = s_i^\epsilon(x, y, t)$

is the arc length along $\Gamma_i(t; \epsilon)$ [7]. By $z_i = r_i/\epsilon$, define $\Phi(z_i, s_i, t; \epsilon) = \phi^\epsilon(x, y, t)$ and $P(z_i, s_i, t; \epsilon) = \hat{\rho}^\epsilon(r_i, s_i, t) = \rho^\epsilon(x, y, t)$ in the inner region. We make explicit the dependence on ϵ of each relevant variable (Q) by expanding $Q = Q^{(0)} + \epsilon Q^{(1)} + \epsilon^2 Q^{(2)} + \dots$ (e.g., $Q = \Phi$); each $Q^{(j)}$ has magnitude of order unity [7].

Our model relies on the continuous functions $\mathfrak{M}(\phi)$, $\zeta(\phi)$ and $\beta(\phi)$ that reconcile the distinct microscale parameters \mathcal{D}_i , k_i^\pm and β_i with the smooth transition of the phase field ϕ^ϵ from each boundary layer to the outer region. Across the boundary layer, the terrace diffusion function \mathfrak{M} (which is a constant in [7]) varies from one diffusivity to another. Since \mathfrak{M} is independent of ϵ , this transition is smooth even in the limit $\epsilon \rightarrow 0$ and does not affect the resulting diffusion equation on terraces. The edge diffusion function $\beta(\phi)$ remains a constant (β_i) in the i th boundary layer; and varies smoothly from β_i to β_{i+1} on the i th terrace. However, this behavior does not alter Eq. (3) because β is multiplied by $|\nabla\phi^\epsilon|$ which vanishes on terraces to leading order in ϵ . The smooth function $\zeta(\phi)$ is properly integrated over the boundary layer to yield the distinct sticking rates ξ_i^\pm . Note that ζ has no effect on any terrace because $\zeta(ia) = 0$ for all i .

We now indicate how the phase field model reduces to the BCF-type theory by skipping algebraic details. For constant parameters, some details are provided in [7]. In the outer region, Eq. (7) yields $G'(\phi^{(0)}) = 0$ to leading order in ϵ ; thus, $\phi^{(0)} = (i-1)a$, ia . This implies that, as $\epsilon \rightarrow 0$, $\Gamma_i(t; 0) \equiv \Gamma_i$ lies between two consecutive terraces of height $(i-1)a$ and ia . Thus, we find $\zeta(\phi^{(0)}) = 0$ and $M(\phi^{(0)}; \epsilon) = \mathcal{D}_i$ on the i th terrace. Hence, Eq. (6) produces Eq. (3) to leading order in ϵ .

In the overlap region near each terrace, every ϕ^ϵ -dependent quantity from the outer region must coincide with the limit of the respective variable from the inner region (boundary layer). For example, as (x, y) approaches Γ_i , $\phi^{(0)}$ from the outer region tends to the limit of $\Phi^{(0)}(z_i, s_i, t)$ as $z_i \rightarrow \pm\infty$; thus, the matching gives $\lim_{z_i \rightarrow -\infty} \Phi^{(0)} = ia$ [7]. Such conditions are incorporated in the inner region as boundary conditions to the appropriate expansions in ϵ of Eqs. (6) and (7).

The ϵ^0 -order of the right-hand side of Eq. (6) reads

$$\begin{aligned} & \kappa_i \mathfrak{M}(\Phi^{(0)}) \partial_{z_i} P^{(0)} \zeta(\Phi^{(0)})^{-1} + \Lambda - \partial_{z_i} \left\{ [\mathfrak{M}(\Phi^{(0)}) \right. \\ & \times (1 + \zeta'(\Phi^{(0)})\Phi^{(1)}) - \mathfrak{M}'(\Phi^{(0)})\zeta(\Phi^{(0)})] \zeta(\Phi^{(0)})^{-2} \partial_{z_i} P^{(0)} \\ & \left. - \mathfrak{M}(\Phi^{(0)}) \partial_{z_i} P^{(1)} \zeta(\Phi^{(0)})^{-1} \right\} - \zeta^2(P^{(0)} + \rho_*). \quad (11) \end{aligned}$$

Note that the term ζ^{-1} grows exponentially as $z_i \rightarrow \pm\infty$. The matching of Eq. (11) with the expected behavior in the outer region implies that such growing terms must be eliminated. Thus, after solving the leading (ϵ^{-1})-order part of Eq. (6) for $\partial_{z_i} P^{(0)}$ ($\partial_{z_i} P^{(0)} \propto \zeta(\Phi^{(0)})$) and substituting the result into Eq. (11), we find that as $z_i \rightarrow \pm\infty$ the limit of $\mathfrak{M}(\Phi^{(0)}) \partial_{z_i} P^{(1)}$ equals the respective limit of

$$\begin{aligned} & \left\{ \left(1 + \zeta'(\Phi^{(0)})\Phi^{(1)} \right) \left[c + \left(\partial_{s_i} \beta_i \partial_{s_i} \kappa_i - \frac{v_i}{a} \right) \frac{\Phi^{(0)}}{a^2} \right] \right\} \\ & = c + a^{-1} (\partial_{s_i} \beta_i \partial_{s_i} \kappa_i - a^{-1} v_i) (i - (1/2 \pm 1/2)), \quad (12) \end{aligned}$$

where c is a constant. The use of the matching condition for the normal flux in the inner and outer region and elimination of c from Eq. (12) yield Eq. (4).

Lastly, to derive Eqs. (5), we integrate the ϵ -expanded Eqs. (6) and (7) over the fast variable (z_i) in the inner region, transform from z_i to ϕ , and apply integration by parts [7]. The evaluation of the boundary terms by use of matching conditions leads to the relation

$$\begin{aligned} & -\hat{\rho}^{(0)} + \rho_* \delta \kappa_i = (-\mathcal{J}_i \cdot \mathbf{n}_i) \\ & \times \int_0^a \frac{\zeta(\Phi + (i-1)a)}{\mathfrak{M}(\Phi + (i-1)a) \sqrt{2G(\Phi)}} \Phi d\Phi \\ & + a^{-2} (\partial_{s_i} \beta_i \partial_{s_i} \kappa_i - a^{-1} v_i) \left[\alpha \rho_* \delta \right. \\ & \left. - \int_0^a \frac{\zeta(\Phi + (i-1)a)}{\mathfrak{M}(\Phi + (i-1)a) \sqrt{2G(\Phi)}} \Phi (a - \Phi) d\Phi \right]; \quad (13) \end{aligned}$$

and a similar expression involving \mathcal{J}_{i-1} . By defining γ_i , p_i and q_i entering $\zeta(\phi)$ so that Eqs. (8)-(10) are satisfied, we obtain Eqs. (5) with the given kinetic rates ξ_i^\pm .

V. CONCLUSION

We presented a phase field model for the near-equilibrium evolution of stepped surfaces with distinct inhomogeneities at the microscale. This work forms an extension of the formulation in [7]. A particular feature of our model, distinct from [7], is the mobility function, $M(\phi^\epsilon)$, that describes sequences of disparate diffusivities, \mathcal{D}_i , and sticking kinetic rates, k_i^\pm , across terraces and steps. Our results can be directly extended to include arc-length-varying step edge diffusivities, $\nu_i(s)$.

Our model has limitations, pointing to open questions. For example, we considered non-interacting steps; the incorporation of entropic and elastic-dipole step-step interactions is a pending issue. The numerical simulation of ϕ^ϵ , although appealing for applications, was not touched upon here. The full continuum limit, where $a \rightarrow 0$ and $\epsilon \rightarrow 0$, was not studied; a germane question is how to implement a reasonable ordering of these limits or scaling of a with ϵ . We expect that the limiting procedure, once carried out, will illuminate the appropriate averaging of material parameters for a macroscopic decorated surface in 2D. This task is left for near-future work.

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