Anisotropic diffusion in continuum relaxation of stepped crystal surfaces

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Abstract

We study the continuum limit in 2+1 dimensions of nanoscale anisotropic diffusion processes on crystal surfaces relaxing to become flat below roughening. Our main result is a continuum law for the surface flux in terms of a new continuum-scale tensor mobility. The starting point is the Burton, Cabrera and Frank (BCF) theory, which offers a discrete scheme for atomic steps whose motion drives surface evolution. Our derivation is based on the separation of local space variables into fast and slow. The model includes: (i) *anisotropic* diffusion of adsorbed atoms (adatoms) on terraces separating steps; (ii) diffusion of atoms along step edges; and (iii) attachment–detachment of atoms at step edges. We derive a parabolic fourth-order nonlinear partial differential equation (PDE) for the continuum surface height profile. An ingredient of this PDE is the surface mobility for the adatom flux, which is a nontrivial extension of the tensor mobility for *isotropic* terrace diffusion derived previously by Margetis and Kohn (2006 *Multisci. Model. Simul.* **5** 729–58). Approximate, separable solutions of the PDE are discussed.

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1. Introduction

Theoretical prediction of crystal surface morphological evolution has been an intensively active area of research for the past several decades. Thanks to advances in computational methods and experimental techniques, our understanding of the microscopic physics driving crystal surface motion continues to improve [1–3]. Considerable attention has been devoted to nanoscale surface structures evolving via surface diffusion. Their stability is crucial for their use as building blocks of novel small devices.

Despite continued progress, basic questions on epitaxial phenomena remain unanswered. In particular, the relation of microscopic physics to continuum laws, e.g., partial differential equations (PDE's) for the surface height profile, is poorly understood.

Features on crystal surfaces evolve differently according to the temperature, T. Below the roughening temperature, T_R, the discrete nature of the crystal is manifested by macroscopically planar surface regions (facets) and distinct nanoscale terraces which separate line defects, steps, of atomic height. The motion of steps drives surface morphological evolution, as first described by Burton, Cabrera and Frank (BCF) [4].

Continuum theories for crystal surfaces below T_R must be the appropriate limits of step motion laws and are challenged near facets [5–7]. By contrast, above T_R steps are created spontaneously and surfaces appear smooth. In this case, continuum laws formulated via thermodynamics and mass conservation are well established [5, 8, 9].

Recently, Margetis and Kohn [10, 11] derived systematically the continuum limit in 2+1 dimensions of a BCF-type model for interacting steps in the absence of material deposition from above. Their formulation incorporates *isotropic* diffusion of adsorbed atoms (adatoms) on terraces and atom attachment–detachment at steps; so, the terrace diffusivity is a scalar. Their analysis invokes separation of local variables into fast and slow. A noteworthy element of the resulting theory is the *tensor* mobility in Fick's law for the adatom flux [10, 11]; the corresponding mobility matrix is diagonal in the step coordinate system. In this setting, the surface relaxes to become flat via an interplay of step energetics and kinetics, and the aspect ratio of step topography brought about by the tensor character of the mobility [11]. Previous continuum theories invoked only a scalar macroscopic mobility, and thus missed the explicit influence of topography on evolution; for a discussion see [10].

In this paper we extend the continuum theory to encompass richer kinetic processes: *anisotropic* adatom diffusion on terraces and atom diffusion *along* step edges. In terrace diffusion, we allow for a non-diagonal diffusivity which explicitly couples adatom fluxes normal and parallel to step edges. Our goal is to derive continuum laws for surface relaxation that correspond more closely to realistic situations. We derive a nonlinear, parabolic fourth-order PDE for the surface height from a large number of coupled differential equations of step motion. In this PDE, the surface mobility tensor has off-diagonal elements in the step coordinate system; further, one of the diagonal elements is directly modified by step edge diffusion. We find plausible scaling laws with time via approximate, separable PDE solutions.

As a starting point, we adopt the BCF model [4] by which individual steps move via mass conservation for atoms. Each step interacts with its nearest neighbors. Accordingly, coupled differential equations are obtained for step positions, which correspond to a discrete scheme. One approach is to solve this scheme numerically. This approach has been followed mainly for one-dimensional geometries [12–14]. Another approach is to view the step flow scheme as a discretization of a continuum evolution equation for the surface height; and *derive* this equation in the appropriate limit of small step height and large number of steps. In this paper we focus on the second approach, which lends itself conveniently to numerics and prediction of decay laws for macroscopic surface features in two space dimensions.

Most previous continuum approaches to crystal surface morphological relaxation invoke isotropic physics for each terrace [10, 15–19]. However, nanoscale anisotropy is almost ubiquitous, and may stem from surface reconstruction and the substrate symmetry and structure [20].

In this paper we focus on terrace diffusion anisotropy, which is characterized by a tensor diffusivity and can influence pattern formation [21]. We do not address anisotropy stemming from the step edge orientation dependence of parameters such as step line tension and stiffness; the macroscopic limit with such parameters is studied in [10]. A transformation that relates

anisotropic adatom diffusion and step edge orientation dependence of step parameters is pointed out in [20]. This last aspect lies beyond our present scope.

We also include step edge diffusion [22–24] for completeness, since edge diffusion may be important in various experimentally accessible systems [1]. In our formalism, the flux along an edge is driven by variations of the step chemical potential, the change per atom in the step energy upon addition or removal of atoms at a step edge. The inclusion of this effect necessarily modifies the surface mobility tensor.

The continuum limit of these processes leads to a generalized relation of the form $\mathbf{J} \propto \mathbf{M} \cdot \nabla \mu$ between the continuum-scale surface flux, $\mathbf{J}$, and the continuum step chemical potential, μ. The coefficient $\mathbf{M}$ is the macroscopic surface mobility. In the curvilinear coordinate system with axes normal and parallel to step edges, $\mathbf{J}$ is

$$\mathbf{J} \propto \begin{pmatrix} M_{11}(|\nabla h|) & M_{12}(|\nabla h|) \\ M_{21}(|\nabla h|) & M_{22}(|\nabla h|) \end{pmatrix} \begin{pmatrix} \partial_{\perp} \mu \\ \partial_{\parallel} \mu \end{pmatrix}. \tag{1}$$

In this relation, M_{ij} are matrix elements of the tensor mobility $\mathbf{M}$ in the local representation, h is the surface height profile, and $\partial_{\perp}$ and $\partial_{\parallel}$ denote space derivatives normal and parallel to step edges where the gradient operator is $\nabla = (\partial_{\perp}, \partial_{\parallel})^T$; cf (52)–(54) of section 3.

In previous works that invoke terrace isotropy in 2+1 dimensions [10, 11], the matrix $\mathbf{M}$ is diagonal in the step coordinate system: $M_{12} = M_{21} = 0$ with $M_{11} \neq M_{22}$ except in the special case of diffusion limited kinetics where $M_{11} = M_{22}$. This form of mobility does not describe experimental situations where hopping of adatoms couples the directions normal and parallel to step edges. This coupling is described by setting $D_{12} = D_{21} \neq 0$ in the diffusivity matrix $\mathbf{D}$, which in turn yields $M_{12} = M_{21} \neq 0$. Here, we determine each M_{ij} explicitly from the step flow model.

There are several critical assumptions inherent to our analysis. Our starting model originates from the mesoscale BCF description where steps are replaced by smooth curves. Hence, we do not consider explicitly atomistic processes which occur at a smaller scale; see e.g. [25]. In our analysis, the terrace width, a microscopic length, is assumed to be much smaller than: (i) the macroscopic length over which the step density varies; (ii) the step radius of curvature; and (iii) the length over which the step curvature varies. Step trains that satisfy (i)–(iii) are referred to as 'slowly varying'. The terrace width is comparable to or larger than the step height so that in the continuum limit the step density approaches the surface slope. We treat monotonic step trains with descending steps and vicinal terraces surrounding a top terrace (peak), and do not address step motion near a bottom terrace (valley).

In an attempt to obtain insights into solutions of the derived parabolic PDE and plausible connections to experiments, we find various scaling laws for the continuum-scale height profile, h. Here, the term 'scaling law' describes the time-dependent part $A(t)$ of a separable solution, $h(\mathbf{r}, t) \approx H(\mathbf{r})A(t)$; see table 1. Note that in principle the initial-boundary value problem for the PDE is not guaranteed to admit separable solutions. This property relies crucially on the initial data. Further, nonlinearities of the PDE can play an important role introducing couplings not captured by scaling scenarios such as ours. We predict scaling laws previously identified for isotropic diffusion [11].

We do not address the numerical solution of the PDE in this paper. A promising approach based on the finite element method when facets are absent is work in progress. Another challenge is to solve the PDE in the presence of facets, where explicit boundary conditions can be available only from discrete simulations [26]. In the same vein, the validity of separable PDE solutions is not studied in the present paper.

We assume that the physics of each terrace, although allowed to be anisotropic, does not vary from one terrace to the next. Hence, our model cannot fully describe 'surface

reconstruction', the situation where adatoms on neighboring terraces adapt differently to the missing bonds at the solid–vapor interface [27, 28]. We have neglected additional complications such as sublimation, material deposition from above, electromigration and elasticity; the last effect may induce long-range, beyond-nearest-neighbor step interactions. The inclusion of these influences in a more general PDE for the surface height in 2+1 dimensions is the subject of future work.

We organize the remainder of the paper as follows. In section 2 we present briefly the BCF model; and summarize a previous derivation [10, 11] of continuum evolution laws from discrete equations of step motion for isotropic diffusion. In section 3 we derive the continuum limit in the case with anisotropic terrace diffusion and step edge diffusion by placing emphasis on the relation between surface flux and step chemical potential. In section 4 we apply approximately separation of variables to the derived PDE. Finally, in section 5 we summarize our results and discuss limitations of our theory.

2. Background: BCF model and PDE with terrace isotropy

In this section we review briefly elements of a previous theory [10, 11] that forms the basis of our analysis. The notation, geometry and methodology outlined here serves section 3 where we consider anisotropic terrace diffusion and step edge diffusion.

We start with the seminal BCF theory [4], which introduced a framework to reconcile the discrete character of crystals in the bulk with the motion of crystal surfaces. In this context, crystal surface evolution is driven by the motion of steps with atomic height, a.

Motion laws for step edges are determined via mass conservation for atoms: the step velocity is the sum of fluxes toward and along an edge. Fluxes result from kinetic processes, including attachment and detachment of atoms at step edges, diffusion of adatoms on terraces and diffusion of atoms along step edges. Equilibrium values in kinetic processes are related to step energetics, namely, the step stiffness and elastic-dipole or entropic step repulsions [1, 29]. We assume that each step interacts only with its nearest neighbors. Beyond-nearest-neighbor elastic dipole interactions only renormalize the step–step interaction strength and thus are not essentially different in the continuum limit [10].

2.1. Step geometry

In the spirit of BCF [4], the edges of steps are projected to closed, noncrossing, and non-self-intersecting smooth curves in a fixed ('basal') reference plane; see figure 1. These curves are treated as moving boundaries for the adatom diffusion of each terrace.

The projection of step edges motivates our choice of local coordinates. The steps are descending and are numbered $i = 1, 2, \ldots, N$, starting from the topmost step ($i = 1$). The basal plane position vector $\mathbf{r}(\eta, \sigma, t) \in \mathbb{R}^2$ is a function of time t and local coordinates η and σ. The variable η identifies the step; $\eta = \eta_i$ for the ith step. The coordinate σ indicates the position along an edge, corresponding to the angle in polar coordinates; for definiteness, σ increases counterclockwise. The unit vectors normal and parallel to step edges are $\mathbf{e}_\eta$ and $\mathbf{e}_\sigma$, which are mutually orthogonal and directed toward increasing η and σ. The associated metric coefficients, which will be needed below when we compute spatial derivatives, are [30]

$$\xi_\eta := |\partial_\eta \mathbf{r}|, \qquad \xi_\sigma := |\partial_\sigma \mathbf{r}|. \tag{2}$$

The step geometry outlined here remains of course unaltered when we consider terrace anisotropy in section 3.
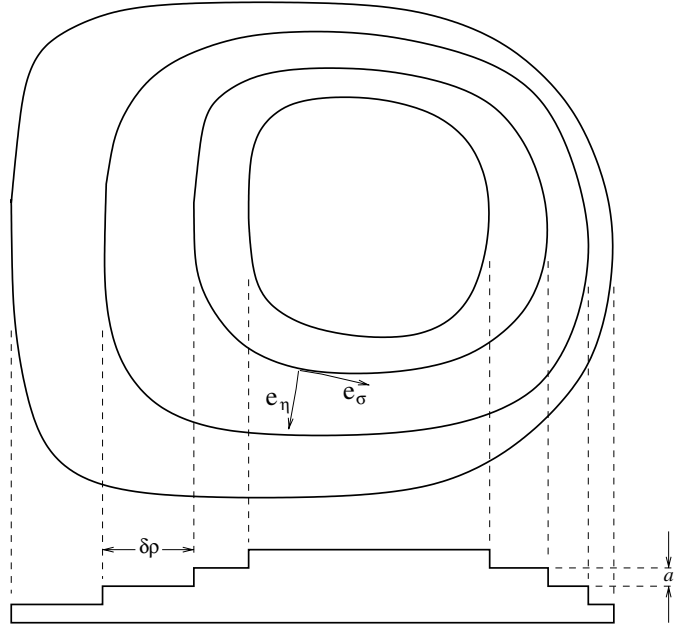
Figure 1. Geometry of steps and terraces near surface peak. Top: projection of step edges to smooth curves on basal plane (top view); unit vectors $\mathbf{e}_\eta$ and $\mathbf{e}_\sigma$ are normal and parallel to step edges. Bottom: side view of step train; a is the constant step height and $\delta\rho$ is typical terrace width.

2.2. BCF model with step interactions in 2+1 dimensions

A quantitative discussion of the BCF theory begins by introducing the adatom density, C_i, on the ith terrace, $\eta_i < \eta < \eta_{i+1}$. This C_i satisfies the diffusion equation,

$$\partial_t C_i = \mathrm{div}(\mathbf{D}^T \cdot \nabla C_i), \tag{3}$$

where $\mathbf{D}^T$ is a tensor (2×2 matrix) diffusivity and $\nabla = \left(\xi_\eta^{-1}\partial_\eta, \xi_\sigma^{-1}\partial_\sigma\right)$ is the gradient on the basal plane. Note that we have omitted from (3) terms that describe atom desorption, electromigration and material deposition from above. A further simplification emerges from the 'quasisteady approximation', $\partial_t C_i \approx 0$, which asserts that the time scale for step motion is much larger than the time scale for terrace diffusion; thus, the time dependence in C_i enters through the boundary conditions at step edges. We define the adatom flux as $\mathbf{J}_i^T = -\mathbf{D}^T \cdot \nabla C_i$.

Robin boundary conditions at the ith and $(i + 1)$th step edges complement (3) to yield a unique solution for C_i. These conditions emerge from linear kinetics [1, 12]:

$$-J_{i,\perp}^T(\eta_i, \sigma, t) = k_u[C_i(\eta_i, \sigma, t) - C_i^{\mathrm{eq}}(\sigma, t)], \tag{4}$$

$$J_{i,\perp}^T(\eta_{i+1}, \sigma', t) = k_d[C_i(\eta_{i+1}, \sigma', t) - C_{i+1}^{\mathrm{eq}}(\sigma', t)], \tag{5}$$

where k_u, k_d are kinetic rates that account for the Ehrlich–Schwoebel barrier [31, 32], $J_{i,\perp}^T(\eta, \sigma, t) := \mathbf{e}_\eta \cdot \mathbf{J}_i^T$ is the transverse component of the adatom flux, and $C_i^{\mathrm{eq}}(\sigma, t)$ is the equilibrium density at the ith step edge.

Next, we express C_i^{eq} as a function of step positions by applying the near-equilibrium thermodynamics law [1, 12]

$$C_i^{\mathrm{eq}}(\sigma) = C_s \exp \frac{\mu_i(\sigma)}{k_B T} \sim C_s \left[1 + \frac{\mu_i(\sigma)}{k_B T}\right], \tag{6}$$

where μ_i is the chemical potential of the ith step. This μ_i depends on the step edge curvature and the energy of interactions with other steps [1, 12, 10]. The linearization in (6) is permissible under typical experimental conditions [33].

The chemical potential μ_i can in principle be given as a function of the step curvature and positions. In [10], μ_i is found with recourse to differential geometry. The result reads

$$\mu_i = \frac{\Omega}{a} \left(\frac{1}{\xi_\eta} \partial_{\eta_i} U_i + \kappa_i U_i \right), \tag{7}$$

where Ω is the atomic volume, U_i is the total energy per length of the ith step edge and κ_i is the step edge curvature. We use the definition [10]

$$U_i = \beta + U_i^{\text{int}}, \tag{8}$$

where β is the step line tension, assumed here to be a constant, and U_i^{int} is the interaction term which in principle depends on the positions $\{\eta_j\}$. For a vicinal surface (i.e., one with sufficiently small slope) and entropic or elastic dipole nearest-neighbor interactions, U_i^{int} is [1, 10, 11, 29]

$$U_i^{\text{int}} = V_{i,i+1} + V_{i,i-1}, \tag{9}$$

$$V_{i,i+1} = \frac{g}{3} m_i^2 \Phi(\rho_i, \rho_{i+1}), \qquad \rho_i := \int_{\eta_0}^{\eta_i} \xi_\eta \, d\eta, \qquad m_i := \frac{a}{\rho_{i+1} - \rho_i}, \tag{10}$$

where g is a positive constant ($g > 0$), ρ_i corresponds to distance in polar coordinates, m_i is the discrete step density, and Φ is a shape factor; note that $\Phi(\rho_i, \rho_i) = \text{const}$ [10].

An important remark is in order. Because C_i^{eq} and μ_i are defined as independent of the kinetic processes, the formulation for the step chemical potential here carries through unaltered when we introduce anisotropic terrace diffusion in section 3.

Lastly, we introduce the step velocity law. By including diffusion of atoms along the step edge with constant edge diffusivity D^E, the normal velocity of the ith step edge is [20, 22–24]

$$v_i = \mathbf{e}_\eta \cdot \frac{d\mathbf{r}_i}{dt} = \frac{\Omega}{a} \left(J_{i-1,\perp}^T - J_{i,\perp}^T \right) + a \partial_s \left(D^E \partial_s \frac{\mu_i}{k_B T} \right), \tag{11}$$

where ∂_s is the space derivative along a step edge; $\partial_s = \xi_\sigma^{-1} \partial_\sigma$. The first term in (11) is the contribution of terrace adatom fluxes. The second term is due to step edge diffusion and stems from the variation of the step chemical potential, μ_i. A reasoning for using μ_i both in edge diffusion and in C_i^{eq} relies on the fact that μ_i controls the equilibrium shape of a step. This equilibrium state is expected to be independent of the kinetic pathway (edge diffusion or attachment-detachment). So, if mass exchange with the terrace is turned off and relaxation occurs via edge diffusion, the step attains the same shape as in the case where edge diffusion is turned off and relaxation is allowed only by attachment-detachment kinetics. This property implies that the thermodynamic driving force has to be the same chemical potential, μ_i, in both cases [34].

Equations (3)–(11) in principle lead to a system of coupled differential equations for the step positions. This system is a discrete scheme of step flow and has been solved numerically for straight and circular interacting steps [12–14]. In this section we focus on (2+1)-dimensional settings with $D^E = 0$.

2.3. Approximations for slowly varying step train

Evidently, the adatom flux $\mathbf{J}_i^T$ plays a pivotal role in connecting the step velocity to the step chemical potential. Next, we find an explicit formula for this flux by solving the diffusion equation (3) approximately following [10].

The key idea is to consider slowly varying step trains and treat the local variables η and σ as fast and slow, respectively. This assumption enables us to neglect the σ derivatives in (3). Accordingly, for constant $\mathbf{D}^T$ the diffusion equation for C_i reduces to

$$\partial_\eta \left(\frac{\xi_\sigma}{\xi_\eta} \partial_\eta C_i \right) \approx 0, \tag{12}$$

which has the explicit solution

$$C_i \approx A_i(\sigma, t) \int_{\eta_i}^{\eta} \frac{\xi_\eta}{\xi_\sigma} \, d\eta' + B_i(\sigma, t) \qquad \eta_i < \eta < \eta_{i+1}, \tag{13}$$

where A_i and B_i are integration constants to be determined via the boundary conditions (4) and (5).

For isotropic adatom diffusion [10] with (scalar) diffusivity D^T the vector-valued adatom flux is computed by

$$\mathbf{J}_i^T = -D^T \nabla C_i. \tag{14}$$

By use of (4) and (5), the flux components restricted at $\eta = \eta_i$ are

$$J_{i,\perp}^T = -\frac{D^T C_s}{k_B T} \frac{1}{\xi_\sigma|_i} \frac{\mu_{i+1} - \mu_i}{D^T \left(\frac{1}{k_u \xi_\sigma|_i} + \frac{1}{k_d \xi_\sigma|_{i+1}} \right) + \int_{\eta_i}^{\eta_{i+1}} \frac{\xi_\eta}{\xi_\sigma} \, d\eta}, \tag{15}$$

$$J_{i,\parallel}^T = -\frac{D^T}{\xi_\sigma|_i} \partial_\sigma \left\{ \frac{D^T \left(\frac{C_{i+1}^{\text{eq}}}{k_u \xi_\sigma|_i} + \frac{C_i^{\text{eq}}}{k_d \xi_\sigma|_{i+1}} \right) + C_i^{\text{eq}} \int_{\eta_i}^{\eta_{i+1}} \frac{\xi_\eta}{\xi_\sigma} \, d\eta}{D^T \left(\frac{1}{k_d \xi_\sigma|_{i+1}} + \frac{1}{k_u \xi_\sigma|_i} \right) + \int_{\eta_i}^{\eta_{i+1}} \frac{\xi_\eta}{\xi_\sigma} \, d\eta} \right\}, \tag{16}$$

where $J_{i,\parallel}^T := \mathbf{e}_\sigma \cdot \mathbf{J}_i^T$. For details on the anisotropic case see section 3.

We pause here to review the assumptions underlying the above approximations. The derivative ∂_σ is treated as $O(\epsilon)$ in comparison to the derivative ∂_η, which is treated as $O(1)$; $\epsilon \ll 1$. It is reasonable to think of ϵ as being of the order of $a\kappa$ where $\kappa = O(\lambda^{-1})$ is a typical step curvature and λ is a suitable macroscopic length [10]. Once the continuum-scale surface flux is derived, the assumptions for the η and σ derivatives are relaxed: both derivatives are allowed to be $O(1)$. An alternative yet equivalent approach based on Taylor expansions at adjacent step edges is described in [11] and in section 3 below.

2.4. Continuum theory with isotropic diffusion in 2+1 dimensions

Step motion laws are viewed as the result of discretizing a PDE for the continuum-scale surface height profile. In this section we review the continuum limit of the discrete model (3)–(11) when the physics of each terrace is isotropic ($\mathbf{D}^T = D^T$: scalar) and there is no step edge diffusion ($D^E = 0$) [10]. Accordingly, we derive a nonlinear fourth-order PDE for the surface height.

First, we summarize the main assumptions made in [10]. The continuum limit corresponds formally to taking $a/\lambda \to 0$ where λ is a macroscopic length. The metric coefficients ξ_σ and ξ_η are $O(\lambda)$, while the terrace width $\delta\rho_i$ is $O(a)$. Therefore, we have $\delta\eta_i = \eta_{i+1} - \eta_i \sim \delta\rho_i \xi_\eta^{-1} = O(a/\lambda) \to 0$. In this limit, we must keep as fixed, $O(1)$ quantities the step density $m_i = a/\delta\rho_i$ and the kinetic parameters $D^T/(k_l a)$ where $l = u$ or d.

The limiting procedure relies on identifying any discrete variable Q_i at a step edge ($\eta = \eta_i$) with the interpolation of a continuous, sufficiently differentiable function $\widetilde{Q}(\eta = \eta_i)$. Thus, $Q_{i+1} - Q_i \approx (\delta\eta_i) \partial_\eta \widetilde{Q}|_i$ where $\mathcal{A}|_i$ denotes $\mathcal{A}(\eta_i)$ throughout. The following assertions

made in [10] carry through for the continuum limit of section 3. (i) The step density approaches the surface slope, $m_i \to m = |\nabla h||_i = O(1)$. (ii) The unit vector normal to the ith step edge becomes $\mathbf{e}_\eta|_i \to \mathbf{e}_\eta = -\frac{\nabla h}{|\nabla h|}$. (iii) The step curvature, $\kappa_i = \nabla \cdot \mathbf{e}_\eta|_i$, approaches $\kappa_i \to \kappa = -\nabla \cdot \left(\frac{\nabla h}{|\nabla h|}\right)$. (iv) The step normal velocity, $v_i = \mathbf{e}_\eta \cdot d\mathbf{r}_i/dt$, becomes $v_i \to v(\mathbf{r}, t) = \frac{\partial_t h}{|\nabla h|}$, the velocity of the level set with height h.

2.4.1. Adatom flux.

Next, we outline the continuum limit of the flux components (15) and (16). The terms on the right-hand sides of these equations are replaced by series expansions as $\delta\eta_i \to 0$.

The resulting continuum limit has the form of a matrix equation involving the adatom mobility $\mathbf{M}^T$, viz.[3],

$$\mathbf{J}_i^T|_i \to \mathbf{J}^T(\mathbf{r}, t) = \begin{pmatrix} J_\perp^T \\ J_\parallel^T \end{pmatrix} = -C_s \mathbf{M}^T \cdot \begin{pmatrix} \partial_\perp \mu \\ \partial_\parallel \mu \end{pmatrix}, \tag{17}$$

where

$$\mathbf{M}^T = \frac{D^T}{k_B T} \begin{pmatrix} \frac{1}{1 + q|\nabla h|} & 0 \\ 0 & 1 \end{pmatrix}, \tag{18}$$

$\partial_\perp = \xi_\eta^{-1}\partial_\eta$, $\partial_\parallel = \xi_\sigma^{-1}\partial_\sigma$ and the kinetic parameter q is defined by

$$q := \frac{2D^T}{ka}, \qquad k^{-1} := \left(k_u^{-1} + k_d^{-1}\right)/2. \tag{19}$$

Equation (17) is complemented with a mass conservation statement for the height profile h and a continuum law for the continuum-scale step chemical potential μ.

2.4.2. Continuum step chemical potential.

Next, we invoke (7)–(10) for the step chemical potential μ_i. Note that we can treat the step edge energy per unit length U_i as the restriction to η_i of a continuous function $\widetilde{U}(\eta)$ [10]. It follows that $\mu_i(\sigma, t) = \frac{\Omega}{a} \text{div}(\widetilde{U}\mathbf{e}_\eta)|_i$.

The continuum step chemical potential $\mu(\mathbf{r}, t)$ is found by taking the continuum limit of (7)–(10). The result is [10] (see footnote 3)

$$\mu_i(t) \to \mu = -\frac{\Omega}{a} \text{div}\left[(\beta + \tilde{g}|\nabla h|^2)\frac{\nabla h}{|\nabla h|}\right], \qquad \tilde{g} := g\Phi(\rho_i, \rho_i) = \text{const.} \tag{20}$$

Note that the definition of μ_i and thus the limit (20) is not affected by the kinetics; thus, (20) remains unaltered by the inclusion of step edge diffusion and terrace diffusion anisotropy.

2.4.3. Mass conservation for adatoms.

For $D^E = 0$ the step velocity law (11) reduces to the usual mass conservation statement for adatoms [10]. Indeed, in the continuum limit the step velocity v_i approaches $\partial_t h/|\nabla h|$. On the other hand, $J_{i-1,\perp}^T|_i$ in the term $J_{i-1,\perp}^T|_i - J_{i,\perp}^T|_i$ of (11) is replaced by an expression involving $\mathbf{J}_{i-1}^T$ evaluated at $\eta = \eta_{i-1}$ through integration of $\text{div}\mathbf{J}_{i-1}^T = 0$ on the $(i-1)$th terrace. This substitution yields a sum that is recognized as a divergence in the continuum limit: the right-hand side of (11) approaches $-\frac{\Omega}{|\nabla h|}\nabla \cdot \mathbf{J}^T$ when $D^E = 0$ [10]. The resulting equation is

$$\partial_t h + \Omega \text{ div } \mathbf{J}^T = 0. \tag{21}$$

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[3] By abusing notation, we use the symbols $\mathbf{J}^T$ and μ to denote the continuum limits of $\mathbf{J}_i^T|_i$ and μ_i, respectively. Strictly speaking, $\mathbf{J}_i^T|_i \to \widetilde{\mathbf{J}}^T(\mathbf{r}, t)$ and $\mu_i(t) \to \widetilde{\mu}(\mathbf{r}, t)$ in the continuum limit.

2.4.4. Evolution equation for surface height. A PDE for the surface height $h(\mathbf{r}, t)$ is found by combination of (17), (20) and (21) [10, 11]:

$$\partial_t h = -B \operatorname{div} \left\{ \mathbf{\Lambda}^T \cdot \nabla \left[\operatorname{div} \left(\frac{\nabla h}{|\nabla h|} + \frac{g_3}{g_1} |\nabla h| \nabla h \right) \right] \right\}, \tag{22}$$

where

$$\mathbf{\Lambda}^T := \frac{k_B T}{D^T} \mathbf{M}^T, \qquad g_1 := \beta/a, \qquad g_3 := \tilde{g}/a, \qquad B := \frac{D^T C_s g_1 \Omega^2}{k_B T}. \tag{23}$$

Evidently, the material parameter B has dimensions (length)^4/time and $\mathbf{\Lambda}^T$ is dimensionless.

3. Anisotropic diffusion

In this section we extend the theory of section 2 to cases with a tensor-valued terrace diffusivity $\mathbf{D}^T$ and a nonzero edge diffusivity D^E, which offer a more realistic description of diffusion processes on terraces and steps. Our goal is to derive a PDE for the surface height. A main ingredient is the surface mobility, which is an extension of (18).

The terrace diffusivity $\mathbf{D}^T$ is assumed to have the tensor form $\mathbf{D}^T = D_{11} \mathbf{e}_\eta \mathbf{e}_\eta + D_{12} \mathbf{e}_\eta \mathbf{e}_\sigma + D_{21} \mathbf{e}_\sigma \mathbf{e}_\eta + D_{22} \mathbf{e}_\sigma \mathbf{e}_\sigma$. For the sake of some generality, we do not enforce the symmetry relation $D_{12} = D_{21}$, although this equality is often dictated on physical grounds. The components of the surface flux $\mathbf{J}_i^T$ are related to both spatial derivatives of the adatom density C_i through the linear relation

$$\begin{pmatrix} J_{i,\perp}^T \\ J_{i,\parallel}^T \end{pmatrix} = - \begin{pmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{pmatrix} \cdot \begin{pmatrix} \xi_\eta^{-1} \partial_\eta C_i \\ \xi_\sigma^{-1} \partial_\sigma C_i \end{pmatrix} \qquad \eta_i < \eta < \eta_{i+1}, \tag{24}$$

assuming that no drift term is present, which would arise from an electromigration current.

3.1. Approximations for fast and slow step variables

In this subsection we provide relations for the adatom flux components at step edges for slowly varying step trains. The starting point is the diffusion equation (3), which becomes

$$\frac{\partial}{\partial \eta} \left(\frac{\xi_\sigma D_{11}}{\xi_\eta} \frac{\partial C_i}{\partial \eta} \right) + \frac{\partial}{\partial \eta} \left(D_{12} \frac{\partial C_i}{\partial \sigma} \right) + \frac{\partial}{\partial \sigma} \left(D_{21} \frac{\partial C_i}{\partial \eta} \right) + \frac{\partial}{\partial \sigma} \left(\frac{\xi_\eta D_{22}}{\xi_\sigma} \frac{\partial C_i}{\partial \sigma} \right) = 0, \tag{25}$$

where $\eta_i < \eta < \eta_{i+1}$. In particular, for slowly varying step train we invoke the separation of the variables (η, σ) into fast and slow as outlined in section 2.4. Hence, (25) reduces to (12), which is solved by (13). By (24), the corresponding flux components are

$$J_{i,\perp}^T \approx -\frac{D_{11}}{\xi_\sigma} A_i(\sigma, t) - \frac{D_{12}}{\xi_\sigma} \partial_\sigma \left[B_i(\sigma, t) + A_i(\sigma, t) \int_{\eta_i}^\eta \frac{\xi_\eta}{\xi_\sigma} \, d\eta' \right], \tag{26}$$

$$J_{i,\parallel}^T \approx -\frac{D_{21}}{\xi_\sigma} A_i(\sigma, t) - \frac{D_{22}}{\xi_\sigma} \partial_\sigma \left[B_i(\sigma, t) + A_i(\sigma, t) \int_{\eta_i}^\eta \frac{\xi_\eta}{\xi_\sigma} \, d\eta' \right]. \tag{27}$$

Equations (26) and (27) are simplified when we evaluate $\mathbf{J}_i^T$ at $\eta = \eta_i$. The resulting matrix equation is

$$-\xi_\sigma|_i \begin{pmatrix} J_{i,\perp}^T|_i \\ J_{i,\parallel}^T|_i \end{pmatrix} = \begin{pmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{pmatrix} \begin{pmatrix} A_i \\ \partial_\sigma B_i \end{pmatrix}. \tag{28}$$

By inspection of (28), the term $\partial_\sigma B_i$ must be treated on equal footing with A_i, since both terms make comparable contributions to the surface flux. We proceed to invert the matrix

equation (28), viewing A_i and $\partial_\sigma B_i$ as integration constants that we have to eliminate from the boundary conditions (4) and (5). Thus, we obtain the formula

$$
\begin{pmatrix} A_i \\ \partial_\sigma B_i \end{pmatrix} = -\frac{\xi_\sigma|_i}{|\mathbf{D}^T|} \begin{pmatrix} D_{22} & -D_{12} \\ -D_{21} & D_{11} \end{pmatrix} \begin{pmatrix} J^T_{i,\perp}|_i \\ J^T_{i,\parallel}|_i \end{pmatrix},
\tag{29}
$$

where $|\mathbf{D}^T| := D_{11}D_{22} - D_{12}D_{21}$ denotes the determinant of $\mathbf{D}^T$.

Next, we apply the boundary conditions (4) and (5) for atom attachment-detachment at step edges. By substituting the solution for the adatom density C_i into these conditions, we find the relations

$$
-J^T_{i,\perp}(\eta_i, \sigma, t) = k_u \big[B_i(\sigma, t) - C_i^{\text{eq}}(\sigma, t) \big]
\tag{30}
$$

$$
J^T_{i,\parallel}(\eta_{i+1}, \sigma', t) = k_d \left[B_i(\sigma', t) + A_i(\sigma', t) \int_{\eta_i}^{\eta_{i+1}} \frac{\xi_\eta}{\xi_\sigma}\, \mathrm{d}\eta - C_{i+1}^{\text{eq}}(\sigma', t) \right].
\tag{31}
$$

We eliminate B_i by setting $\sigma' = \sigma$ in equation (31), multiplying (30) by k_d/k_u and subtracting the resulting equation from (31). Substituting for A_i from (29), we arrive at the first desired relation between the surface flux components:

$$
\left(\frac{1}{k_u} + \frac{\xi_\sigma|_i D_{22}}{|\mathbf{D}^T|} \int_{\eta_i}^{\eta_{i+1}} \frac{\xi_\eta}{\xi_\sigma}\, \mathrm{d}\eta \right) J^T_{i,\perp}|_i + \frac{1}{k_d} J^T_{i,\perp}|_{i+1}
$$
$$
- \frac{\xi_\sigma|_i D_{12}}{|\mathbf{D}^T|} \left(\int_{\eta_i}^{\eta_{i+1}} \frac{\xi_\eta}{\xi_\sigma}\, \mathrm{d}\eta \right) J^T_{i,\parallel}|_i = C_i^{\text{eq}} - C_{i+1}^{\text{eq}}.
\tag{32}
$$

We obtain a second relation by exploiting variations in σ, which can be taken to be arbitrarily small; in contrast, changes in η are restricted by a and the requirement of finite slope. Therefore, we differentiate (30) with respect to σ and substitute for $\partial_\sigma B_i$ from (29). Subsequently, we neglect $\partial_\sigma J^T_{i,\perp}$, consistent with the hypothesis of slowly varying step edge curvature. Thus, the second desired relation of the flux components reads

$$
\frac{\xi_\sigma|_i}{|\mathbf{D}^T|} \big(D_{21} J^T_{i,\perp}|_i - D_{11} J^T_{i,\parallel}|_i \big) - \partial_\sigma C_i^{\text{eq}} = 0,
$$

which in turn becomes

$$
D_{21} J^T_{i,\perp}|_i - D_{11} J^T_{i,\parallel}|_i = \frac{C_s |\mathbf{D}^T|}{\xi_\sigma|_i} \frac{\partial_\sigma \mu_i}{k_B T} = \frac{C_s |\mathbf{D}^T|}{k_B T} \partial_\parallel \mu_i.
\tag{33}
$$

Equations (32) and (33) suffice for the purpose of taking the continuum limit.

3.2. Continuum-scale adatom flux

In this subsection we derive the analogue of (17) and (18), the relation between continuum adatom flux and step chemical potential. The resulting terrace mobility, $\mathbf{M}^T$, will still need modification to account for step edge diffusion.

First, we simplify relations (32) and (33) for $\mathbf{J}^T_i$. Considering $\delta\eta_i = \eta_{i+1} - \eta_i$ as small, we make the approximations

$$
\frac{1}{k_u} J^T_{i,\perp}|_i + \frac{1}{k_d} J^T_{i,\perp}|_{i+1} = \left(\frac{1}{k_u} + \frac{1}{k_d} \right) J^T_{i,\perp}|_i [1 + O(\delta\eta_i)],
\tag{34}
$$

$$
\int_{\eta_i}^{\eta_{i+1}} \frac{\xi_\eta}{\xi_\sigma}\, \mathrm{d}\eta = \frac{\xi_\eta|_i}{\xi_\sigma|_i} \delta\eta_i [1 + O(\delta\eta_i)].
\tag{35}
$$

We consolidate the kinetic rates k_u, k_d into the parameter $k = 2/(k_u^{-1} + k_d^{-1})$ of (19). Thus, (32) reduces to

$$\left[\left(\frac{2}{k} + \frac{\xi_\eta|_i D_{22}}{|\mathbf{D}^T|}\delta\eta_i\right) J_{i,\perp}^T\big|_i - \frac{\xi_\eta|_i D_{12}}{|\mathbf{D}^T|}\delta\eta_i J_{i,\parallel}^T\big|_i\right][1 + O(\delta\eta_i)] = C_i^{\text{eq}} - C_{i+1}^{\text{eq}}. \qquad (36)$$

We multiply (36) by $|\mathbf{D}^T|/(\xi_\eta|_i\delta\eta_i)$ and thereby obtain

$$\left(D_{22} + \frac{2|\mathbf{D}^T|}{k\xi_\eta|_i\delta\eta_i}\right) J_{i,\perp}^T\big|_i - D_{12}J_{i,\parallel}^T\big|_i = |\mathbf{D}^T|\frac{C_i^{\text{eq}} - C_{i+1}^{\text{eq}}}{\xi_\eta|_i\delta\eta_i}. \qquad (37)$$

As $\delta\eta_i \to 0$, the right-hand side of (37) approaches $C_s|\mathbf{D}^T|\partial_\perp\mu/k_BT$. On the other hand, the ratio of parameters in the prefactor of $J_{i,\perp}^T|_i$ has the limiting value

$$\frac{2|\mathbf{D}^T|}{k\xi_\eta|_i\delta\eta_i} \to \frac{2|\mathbf{D}^T|}{ka}|\nabla h| = \mathcal{D}^T|\nabla h|, \qquad \mathcal{D}^T := \frac{2|\mathbf{D}^T|}{ka}, \qquad (38)$$

where $\mathcal{D}^T$ has dimensions of diffusivity [(length)^2/time].

A matrix equation for the continuum-scale surface flux $\mathbf{J}^T = (J_\perp^T, J_\parallel^T)^T$ in terms of the step chemical potential μ comes from combining (33), (37) and (38):

$$\begin{pmatrix} D_{22} + \mathcal{D}^T|\nabla h| & -D_{12} \\ -D_{21} & D_{11} \end{pmatrix}\begin{pmatrix} J_\perp^T \\ J_\parallel^T \end{pmatrix} = -\frac{C_s|\mathbf{D}^T|}{k_BT}\begin{pmatrix} \partial_\perp\mu \\ \partial_\parallel\mu \end{pmatrix}. \qquad (39)$$

By solving (39) for $\mathbf{J}^T$ we obtain

$$\mathbf{J}_i^T\big|_i \to \mathbf{J}^T(\mathbf{r}, t) = \begin{pmatrix} J_\perp^T \\ J_\parallel^T \end{pmatrix} = -C_s\mathbf{M}^T \cdot \begin{pmatrix} \partial_\perp\mu \\ \partial_\parallel\mu \end{pmatrix}, \qquad (40)$$

where the continuum-scale adatom mobility is

$$\mathbf{M}^T = \frac{1}{k_BT\,(1 + q|\nabla h|)}\begin{pmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} + \mathcal{D}^T|\nabla h| \end{pmatrix}, \qquad q := \frac{2D_{11}}{ka}. \qquad (41)$$

This formula reduces to the equation with diagonal $\mathbf{M}^T$ found in [10] when $D_{11} = D_{22} = D^T$ and $D_{12} = D_{21} = 0$; cf (18). In contrast to the case with scalar diffusivity, all matrix elements of the mobility in (41) depend on the slope. This dependence is quite pronounced in the kinetic regime of attachment-detachment limited (ADL) kinetics, which we discuss in section 4.

3.3. Alternative approach to continuum: Taylor expansions

For the sake of completeness, we re-derive (40) and (41) via an alternative yet equivalent route. This is based on expansions of the boundary conditions (4) and (5) for atom attachment-detachment in appropriate Taylor series when $\delta\eta_i = \eta_{i+1} - \eta_i \to 0$ and $\delta\sigma = \sigma' - \sigma \to 0$.

Following the derivation outlined by one of us in a letter [11], we first expand $C_i|_{i+1}$ and $J_{i,\perp}^T|_{i+1}$ in (5) to first order in $\delta\sigma$ and $\delta\eta_i$:

$$k_u\left(J_{i,\perp}^T\big|_i + \partial_\eta J_{i,\perp}^T\big|_i\delta\eta_i + \partial_\sigma J_{i,\perp}^T\big|_i\delta\sigma\right) = k_uk_d\left[C_i|_i + \partial_\eta C_i|_i\delta\eta_i + \partial_\sigma C_i|_i\delta\sigma - C_i^{\text{eq}}(\sigma + \delta\sigma, t)\right]. \qquad (42)$$

Second, we multiply (4) by k_d and subtract the resulting equation from (42), so as to eliminate C_i. By neglecting the η- and σ-derivatives of $J_{i,\perp}^T$, we find

$$(k_u + k_d)J_{i,\perp}^T\big|_i = k_uk_d\left\{\partial_\eta C_i|_i\delta\eta_i + \partial_\sigma C_i|_i\delta\sigma - \frac{C_s}{k_BT}[\mu(\eta_{i+1}, \sigma + \delta\sigma) - \mu(\eta_i, \sigma)]\right\}. \qquad (43)$$

Next, we solve for $\partial_\eta C_i$ and $\partial_\sigma C_i$ by applying the matrix equation (24). The substitution of $\partial_\eta C_i$ and $\partial_\sigma C_i$ into (43) and subsequent expansion of the difference $\mu(\eta_{i+1}, \sigma + \delta\sigma) - \mu(\eta_i, \sigma)$ about (η_i, σ) yields a relation between $\mathbf{J}_i^T$ and the gradient of the continuum step chemical potential $\mu(\mathbf{r}, t)$:

$$\left(\frac{1}{k_u} + \frac{1}{k_d} + \frac{D_{22}\xi_\eta \delta\eta_i}{|\mathbf{D}^T|} \right) J_{i,\perp}^T|_i - \frac{\xi_\eta D_{12}\delta\eta_i}{|\mathbf{D}^T|} J_{i,\parallel}^T|_i + \frac{C_s}{k_B T}\partial_\eta \mu|_i \delta\eta_i$$
$$= \left[\frac{\xi_\sigma}{|\mathbf{D}^T|}\left(D_{12}J_{i,\perp}^T - D_{11}J_{i,\parallel}^T\right)|_i - \frac{C_s}{k_B T}\partial_\sigma \mu|_i \right]\delta\sigma. \tag{44}$$

Setting $\delta\sigma = 0$ in (44) and taking the continuum limit provides our first equation for the components of the surface flux in terms of μ :

$$\left(1 + \frac{2|\mathbf{D}^T|}{ka D_{22}}|\nabla h| \right) J_\perp^T - \frac{D_{12}}{D_{22}} J_\parallel^T = -\frac{C_s|\mathbf{D}^T|}{k_B T D_{22}}\partial_\perp \mu. \tag{45}$$

The continuum limit of (44) still applies when $\delta\sigma \neq 0$. By (45), we know that the left-hand side of (44) tends to zero in that limit. Therefore, the term proportional to $\delta\sigma$ must also vanish as $\delta\eta_i \to 0$. Thus, we have

$$D_{21}J_\perp^T - D_{11}J_\parallel^T = \frac{C_s|\mathbf{D}^T|}{k_B T}\partial_\parallel \mu. \tag{46}$$

By solving simultaneously (45) and (46) for the components of the continuum surface flux, we find

$$\begin{pmatrix} J_\perp^T \\ J_\parallel^T \end{pmatrix} = \frac{-C_s}{k_B T\,(1 + q|\nabla h|)}\begin{pmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} + \mathcal{D}^T|\nabla h| \end{pmatrix}\cdot\begin{pmatrix} \partial_\perp \mu \\ \partial_\parallel \mu \end{pmatrix}, \tag{47}$$

which is directly identified with the combination of (40) and (41).

3.4. Mass conservation law and total surface flux

In this subsection we define the *total* surface flux $\mathbf{J}$ so that the mass conservation law for atoms is satisfied in the presence of step edge diffusion. The surface mobility is defined accordingly through the relation of $\mathbf{J}$ and μ.

At a given location σ on the ith step edge, the step normal velocity v_i must respect conservation of mass, taking into account all possible sources and sinks of atoms; see (11). By section 2.4.3, in the continuum limit (11) reduces to

$$\partial_t h = -\Omega\nabla\cdot\mathbf{J}^T + \frac{a|\nabla h|}{\xi_\sigma}\partial_\sigma\left\{ \frac{D^E}{\xi_\sigma}\partial_\sigma\left(\frac{\mu}{k_B T} \right) \right\}, \tag{48}$$

where the adatom flux $\mathbf{J}^T$ is described by (40) and (41).

Since the terrace is a level set for the height, we have $h = H(\eta, t)$; in other words, h does not vary in the step-longitudinal (σ-) direction. Thus, $|\nabla h| = \xi_\eta^{-1}|\partial_\eta H|$ and the factor $|\partial_\eta H|$ can be passed through the σ derivative in (48). It follows that

$$\partial_t h = -\Omega\nabla\cdot\mathbf{J}^T + \frac{1}{\xi_\eta\xi_\sigma}\partial_\sigma\left\{ aD^E|\nabla h|\frac{\xi_\eta}{\xi_\sigma}\partial_\sigma\left(\frac{\mu}{k_B T} \right) \right\}. \tag{49}$$

We recognize the second term on the right-hand side of (49) as the divergence of $aD^E|\nabla h|\partial_\parallel(\mu/k_B T)\,\mathbf{e}_\sigma$. Hence, we refer to the term $-\frac{aD^E}{\Omega}|\nabla h|\partial_\parallel(\mu/k_B T)\,\mathbf{e}_\sigma$ as the edge atom flux, denoted by $\mathbf{J}^E$. Combining the two divergence terms into one term, we obtain the mass conservation law

$$\partial_t h = -\Omega\nabla\cdot(\mathbf{J}^T + \mathbf{J}^E) = -\Omega\nabla\cdot\mathbf{J}, \tag{50}$$

where

$$\mathbf{J} = \mathbf{J}^T + \mathbf{J}^E, \qquad \mathbf{J}^E := -\frac{aD^E}{\Omega}|\nabla h|\partial_\parallel\left(\frac{\mu}{k_B T}\right)\mathbf{e}_\sigma. \tag{51}$$

Thus, the matrix equation (47) involving the mobility tensor can be updated accordingly for the effective surface flux:

$$\mathbf{J}(\mathbf{r}, t) = \begin{pmatrix} J_\perp \\ J_\parallel \end{pmatrix} = -C_s \begin{pmatrix} M_{\eta\eta} & M_{\eta\sigma} \\ M_{\sigma\eta} & M_{\sigma\sigma} \end{pmatrix} \cdot \begin{pmatrix} \partial_\perp \mu \\ \partial_\parallel \mu \end{pmatrix} = -C_s \mathbf{M} \cdot \nabla\mu, \tag{52}$$

where

$$\mathbf{M} = \begin{pmatrix} M_{\eta\eta} & M_{\eta\sigma} \\ M_{\sigma\eta} & M_{\sigma\sigma} \end{pmatrix}, \tag{53}$$

$$M_{\eta\eta} = \frac{D_{11}/(k_B T)}{1 + 2\frac{D_{11}}{ka}|\nabla h|}, \qquad M_{\eta\sigma} = \frac{D_{12}/(k_B T)}{1 + 2\frac{D_{11}}{ka}|\nabla h|},$$

$$M_{\sigma\eta} = \frac{D_{21}/(k_B T)}{1 + 2\frac{D_{11}}{ka}|\nabla h|}, \qquad M_{\sigma\sigma} = \frac{1}{k_B T}\frac{D_{22} + \frac{2|\mathbf{D}^T|}{ka}|\nabla h|}{1 + 2\frac{D_{11}}{ka}|\nabla h|} + \frac{aD^E}{\Omega C_s}|\nabla h|. \tag{54}$$

In applications it is often desirable to represent the total mobility tensor $\mathbf{M}$ with respect to a fixed coordinate system. We invoke the similarity transformation outlined in [10] in order to obtain the basal plane's Cartesian representation of $\mathbf{M}$. Using the change-of-basis matrix

$$\mathbf{S} = |\nabla h|^{-1}\begin{pmatrix} -\partial_x h & \partial_y h \\ -\partial_y h & -\partial_x h \end{pmatrix}, \tag{55}$$

we obtain the representation

$$\mathbf{M}_{(x,y)} = \mathbf{SMS}^{-1} = \frac{\widetilde{M}_{xx}\mathbf{e}_x\mathbf{e}_x + \widetilde{M}_{xy}\mathbf{e}_x\mathbf{e}_y + \widetilde{M}_{yx}\mathbf{e}_y\mathbf{e}_x + \widetilde{M}_{yy}\mathbf{e}_y\mathbf{e}_y}{k_B T|\nabla h|^2\left(1 + \frac{2D_{11}}{ka}|\nabla h|\right)}, \tag{56}$$

where

$$\widetilde{M}_{xx} := D_{11}(\partial_x h)^2 - (D_{12} + D_{21})(\partial_x h)(\partial_y h) + \left[(D_{22} + \mathcal{D}^T|\nabla h|)\right.$$
$$\left. + \frac{aD^E}{\Omega C_s}|\nabla h|\left(1 + \frac{2D_{11}}{ka}|\nabla h|\right)\right](\partial_y h)^2, \tag{57}$$

$$\widetilde{M}_{xy} := D_{12}(\partial_x h)^2 - D_{21}(\partial_y h)^2 + \left[D_{11} - (D_{22} + \mathcal{D}^T|\nabla h|)\right.$$
$$\left. - \frac{aD^E}{\Omega C_s}|\nabla h|\left(1 + \frac{2D_{11}}{ka}\right)\right](\partial_x h)(\partial_y h), \tag{58}$$

$$\widetilde{M}_{yx} = D_{21}(\partial_x h)^2 - D_{12}(\partial_y h)^2 + \left[D_{11} - (D_{22} + \mathcal{D}^T|\nabla h|)\right.$$
$$\left. - \frac{aD^E}{\Omega C_s}|\nabla h|\left(1 + \frac{2D_{11}}{ka}\right)\right](\partial_x h)(\partial_y h), \tag{59}$$

$$\widetilde{M}_{yy} = \left[(D_{22} + \mathcal{D}^T|\nabla h|) + \frac{aD^E}{\Omega C_s}|\nabla h|\left(1 + \frac{2D_{11}}{ka}|\nabla h|\right)\right](\partial_x h)^2$$
$$+ (D_{12} + D_{21})(\partial_x h)(\partial_y h) + D_{11}(\partial_y h)^2. \tag{60}$$

So far, we derived a relation of the form $\mathbf{J} = -C_s \mathbf{M} \cdot \nabla \mu$ for the surface flux where $\partial_t h = -\Omega \, \mathrm{div} \, \mathbf{J}$. The chemical potential μ is related to derivatives of h through (20).

3.5. PDE for height profile

We now combine the mass conservation law (50) with the effective surface flux (52) and the formula for the continuum step chemical potential (20) in order to derive a PDE analogous to (22) for the surface height profile, $h(\mathbf{r}, t)$. With the substitutions for μ and $\mathbf{J}$ by (20) and (52), the mass conservation law (50) becomes

$$\partial_t h = -\frac{\Omega^2 C_s}{a} \, \mathrm{div} \left\{ \mathbf{M} \cdot \nabla \left(\mathrm{div} \left[(\beta + \tilde{g} |\nabla h|^2) \frac{\nabla h}{|\nabla h|} \right] \right) \right\}. \tag{61}$$

To consolidate the physical parameters, we define $g_1 = \beta/a$, $g_3 = \tilde{g}/a$, and $B = \Omega^2 C_s g_1$; see (23). Accordingly, we obtain (22) with $\mathbf{M}^T$ replaced by the effective total mobility $\mathbf{M}$.

4. Scaling laws

In this section we derive approximate, separable solutions of PDE (61). Our goal is to find plausible connections of actual continuum solutions to decay laws observed in biperiodic profiles, e.g. observations reported in [35–38]. Our discussion is heuristic; the relation of PDE solutions to experiments is not well understood at the moment.

We start with the ansatz $h(\mathbf{r}, t) \approx A(t) H(\mathbf{r})$. This separation of variables, called a 'scaling ansatz', is consistent with previously reported step flow simulations in 1D [13] and kinetic Monte Carlo simulations in 2D [18], both with initial sinusoidal profiles. The amplitude $A(t)$ can be obtained formally from an ordinary differential equation (ODE) by direct substitution in (61). We alert the reader that conditions on the initial data and material parameters for having separable solutions and recovering an ODE for A are currently elusive, requiring detailed numerical studies. Such studies lie beyond our present scope.

Additive terms in the driving force $\nabla \mu$ and in the total mobility $\mathbf{M}$ scale differently with A. We need to retain in the right-hand side of the PDE terms proportional to the same power of A and thus resort to approximations. It should be borne in mind that the nonlinearities in $\mathbf{M}$ and μ lead to spatial-frequency coupling for biperiodic height profiles; accordingly, evolution is in principle more complicated than that implied here by our simple scaling scenario.

Depending on the powers of A that possibly prevail in the evolution equation, we find several plausible behaviors of h with time, including the exponential decay and inverse linear decay reported in related experiments [35–38]. By (20) the driving force $\nabla \mu$ scales as A^0 if the dominant term is step line tension. If step interactions are dominant, then $\nabla \mu$ scales as A^2. To determine the scaling of the mobility tensor, it is convenient to introduce the 'aspect ratio' $\alpha := \partial_y h / \partial_x h$; it is plausible yet not compelling to estimate α by λ_x / λ_y where λ_x and λ_y are wavelengths in the x and y directions. We also define the slope-dependent quantity $b := (1 + \frac{2D_{11}}{ka} |\nabla h|)^{-1}$. Note that α scales as A^0. When step edge diffusion is absent ($D^E = 0$), the possible scalings found for A with nonzero D_{12} and D_{21} are not different from those for isotropic adatom diffusion (where $D_{12} = D_{21} = 0$) [11].

With these definitions, the elements $M_{ij} = (k_B T)^{-1} |\nabla h|^{-2} b \widetilde{M}_{ij}$ ($i, j = x, y$) from the Cartesian representation (57)–(60) of $\mathbf{M}$ read

$$M_{xx} = \frac{b(\partial_x h)^2}{k_B T |\nabla h|^2} \left[D_{11} - \alpha(D_{12} + D_{21}) + \alpha^2 D_{22} + \frac{2|\mathbf{D}^T|}{ka} \alpha^2 |\nabla h| + \frac{a D^E \alpha^2 |\nabla h|}{b \Omega C_s} \right],$$

$$M_{xy} = \frac{b(\partial_x h)^2}{k_B T |\nabla h|^2} \left[D_{12} + \alpha(D_{11} - D_{22}) - \alpha^2 D_{21} - \frac{2|\mathbf{D}^T|}{ka} \alpha |\nabla h| - \frac{a D^E \alpha |\nabla h|}{b \Omega C_s} \right],$$

$$M_{yx} = \frac{b(\partial_x h)^2}{k_B T |\nabla h|^2} \left[D_{21} + \alpha(D_{11} - D_{22}) - \alpha^2 D_{12} - \frac{2|\mathbf{D}^T|}{ka}\alpha|\nabla h| - \frac{a D^E \alpha |\nabla h|}{b\Omega C_s} \right],$$

$$M_{yy} = \frac{b(\partial_x h)^2}{k_B T |\nabla h|^2} \left[D_{22} + \alpha(D_{12} + D_{21}) + \alpha^2 D_{11} + \frac{2|\mathbf{D}^T|}{ka}|\nabla h| + \frac{a D^E |\nabla h|}{b\Omega C_s} \right].$$

$$(62)$$

We restrict attention to ADL kinetics which closely correspond to relevant experimental situations [35–38]. It follows that $b \ll 1$ where b scales as A^{-1}; by the scaling ansatz for h, the prefactor $\frac{b(\partial_x h)^2}{k_B T |\nabla h|^2}$ also scales as A^{-1}. For the sake of simplicity we consider weak anisotropy, $|\mathbf{D}^T| \approx D_{11} D_{22}$ (i.e., if the off-diagonal diffusivity elements D_{12}, D_{21} are small in comparison to the diagonal elements) and $|\mathbf{D}^T|/(ka) \gg a D^E/(b\Omega C_s)$. The dominant terms in $\mathbf{M}$ scale as

(i) A^0 if $b \ll \min\{(D_{22}/D_{11})\alpha^2, (D_{22}/D_{11})\alpha^{-2}, D_{22}/D_{11}\}$; and
(ii) A^{-1} if $b \gg \max\{(D_{22}/D_{11})\alpha^2, (D_{22}/D_{11})\alpha^{-2}, D_{22}/D_{11}\}$.

In the presence of step edge diffusion with $|\mathbf{D}^T|/(ka) \ll a D^E/(b\Omega C_s)$, the dominant terms in the mobility tensor scale as A^1. Note that in all these cases the matrix $\mathbf{M}$ tends to become singular since the lowest eigenvalue acquires a small value. Hence, correction terms in $\mathbf{M}$, which strictly spoil the scalings reported here, are physically important; solutions of the form $A(t)H(\mathbf{r})$ should be thought of as leading-order terms of appropriate asymptotic expansions for h.

Next, we combine the three possible scalings of $\mathbf{M}$ with the two possible scalings of $\nabla\mu$. Each combination yields an ODE of the form $\dot{A} \propto -A^p$ for some exponent p; the minus sign here is assumed for achieving profile decay. In the case of ADL kinetics, outlined above, we have $p \in \{-1, 0, 1\} \cup \{1, 2, 3\}$, where the first set corresponds to dominant step line tension and the second set corresponds to dominant step interactions in $\nabla\mu$. Since $p = 1$ is common to both sets, the associated scaling law $A = A_0 \exp(-t/\tau)$ could perhaps be observed in a wide range of experimental situations. On the other hand, the scaling law $A = A_0/\sqrt{1 + t/\tau}$ associated with $p = 3$ and dominance of step edge diffusion may not be physical; to our knowledge, this last decay law has not been observed.

We illustrate the procedure of finding A for weak anisotropy under condition (ii) above and dominant step interactions; thus, $p = 1$. The PDE has the form

$$\dot{A}(t)H(\mathbf{r}) \propto -A(t)\,\mathrm{div}\left\{ \frac{(\partial_x H)^2}{|\nabla H|^3} \begin{pmatrix} m_{xx} & m_{xy} \\ m_{yx} & m_{yy} \end{pmatrix} \cdot \nabla[\mathrm{div}(|\nabla H|\nabla H)] \right\}, \quad (63)$$

where the prefactor is positive and the elements $\{m_{ij}\}_{i,j=x}^y$ are constants that stem from $\mathbf{M}_{(x,y)}$ after factoring out A (but not H); the precise definition of m_{ij} is omitted here.

To satisfy (63) for all t and $\mathbf{r}$, we require that the time-dependent part $A(t)$ solve $\dot{A}(t) = -\mathcal{C}A$ for some positive constant $\mathcal{C}$ ($\mathcal{C} > 0$). The height profile $H(\mathbf{r})$ solves a nonlinear PDE of the form

$$\mathcal{C}H \propto \mathrm{div}\left\{ \frac{(\partial_x H)^2}{|\nabla H|^3} \begin{pmatrix} m_{xx} & m_{xy} \\ m_{yx} & m_{yy} \end{pmatrix} \cdot \nabla[\mathrm{div}(|\nabla H|\nabla H)] \right\}. \quad (64)$$

The solution for $A(t)$ is given in terms of the separation constant $\mathcal{C}$ and the initial amplitude A_0: $A(t) = A_0 \mathrm{e}^{-\mathcal{C}t}$. Using a similar procedure, we derive other possible scaling laws for ADL kinetics under different restrictions. Our results are summarized in table 1.

We do not address the issue of solving (64) in this analysis. Particularly interesting is the case with facets. The continuum limit breaks down at facet edges and associated boundary conditions for H must take into account the discrete step flow equations [26]. A numerical scheme to implement these boundary conditions within continuum is still under development.

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Table 1. Decay laws for height amplitude $A(t)$ in ADL kinetics. The leftmost column indicates plausible conditions. The next two columns list decay laws for line tension and step interaction dominated $\nabla\mu$. The time constant τ depends on $A(0)$ and H.

	Line tension	Step interaction
$\|\mathbf{D}^T\| \approx D_{11}D_{22}$ $b \gg \max\{(D_{22}/D_{11})\alpha^2, D_{22}/D_{11}, (D_{22}/D_{11})\alpha^{-2}\}$ $b \ll \min\{D_{22}/D_{11})\alpha^2, D_{22}/D_{11}, (D_{22}/D_{11})\alpha^{-2}\}$	$A_0\sqrt{1-t/\tau}$ $A_0(1-t/\tau)$	$A_0\exp(-t/\tau)$ $A_0/(1+t/\tau)$
$\|\mathbf{D}^T\|/(ka) \ll aD^E/(b\Omega C_s)$	$A_0\exp(-t/\tau)$	$A_0/\sqrt{1+t/\tau}$

A similar analysis can be carried out if terrace diffusion is the slowest process, i.e., $q|\nabla h| = |\nabla h|D_{11}/(ka) \ll 1$. Then, b is approximately a constant, $b \approx 1$. The dominant terms in the mobility tensor scale as A^0 or A^1. Thus, we obtain $\dot{A} \propto -A^p$ for $p \in \{0, 1, 2, 3\}$, which yields four of the five decay laws already found for ADL kinetics.

5. Conclusion

By interpreting a (2+1)-dimensional step flow model for a relaxing surface as a discretization of a continuum evolution equation, we derived the relevant PDE for the surface height profile. The starting point is a step velocity law that accounts for anisotropic adatom diffusion on terraces, diffusion of atoms along step edges and atom attachment-detachment at steps. In the continuum limit we obtained a relation between the surface flux and the step chemical potential. This relation involves a tensor surface mobility as an effective coefficient.

We gave two different derivations of the surface mobility under the assumption of linear kinetics at step edges. Our main approach relies on the direct solution of the diffusion equation for adatoms on each terrace via the separation of local step coordinates into fast and slow. The continuum limit is attained by letting the step height and terrace widths tend to zero under the condition that the slope remains finite.

Combining the step velocity law with the continuum relation between the surface flux and the step chemical potential resulted in a nonlinear, fourth-order parabolic PDE for the surface height. Transforming the mobility tensor from local step coordinates to fixed coordinates induced a dependence on the height partial derivatives. This dependence offers a plausible scenario of how an epitaxial surface can exhibit different decay laws. We found separable solutions for the height that approximately satisfy the evolution equation under certain conditions. These separable solutions exhibit different decay and may be used as a guide in interpreting experimental observations from a continuum viewpoint.

Our PDE only accounts for a part of the possible microscopic physics. We neglected elasticity which may induce long-range interactions between steps, surface reconstruction, material deposition, and evaporation/condensation (sublimation). Incorporating these processes into the theory is work in progress. For example, the inclusion of evaporation/ condensation requires only an additive term in the step velocity law [17]. The continuum limit with this additional effect is already within the scope of the analysis presented here. More challenging is the inclusion of processes that modify (i) the terrace diffusion equation; (ii) the kinetic boundary conditions at step edges; and (iii) the formula for the step chemical potential.

The tensor mobility depends crucially on the kinetics of each terrace. More general mobility tensors might emerge by encompassing terms that account for (i)–(iii) above. With the inclusion of step edge diffusion, which was absent from previous derivations of a tensor

mobility [10, 11], we found an effective mobility whose elements still depend only on $|\nabla h|$; even then, the mobility **M** does not involve powers of $|\nabla h|$ greater than 1. We plan to investigate the possible structure of **M** in more general physical settings.

The PDE we derived for the surface height may admit separable solutions under certain conditions, which are not precisely known at the moment. We hope to make connections to experiments on surface relaxation with anisotropic diffusivity. One challenge in making these comparisons is to single out experimentally measurable quantities that correspond to PDE solutions in an appropriate sense. Another challenge in this context is the incorporation of facets within a viable scheme of solving the PDE. The theory presented here can serve as a basis for future work, in which the PDE for surface height evolution is implemented numerically for comparisons with experimental data.

Acknowledgments

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