PHYSICAL REVIEW B **75**, 165409 (2007)

Possible mechanism for the onset of step-bunching instabilities during the epitaxy of single-species crystalline films

Paolo Cermelli*
Dipartimento di Matematica, Università di Torino, Via Carlo Alberto 10, 10123 Torino, Italy

Michel E. Jabbour†
Department of Mathematics, University of Kentucky, Lexington, Kentucky 40506-0027, USA

(Received 7 September 2006; revised manuscript received 8 December 2006; published 13 April 2007)

A thermodynamically consistent continuum theory for single-species, step-flow epitaxy that extends the classical Burton-Cabrera-Frank (BCF) framework is derived from basic considerations. In particular, an expression for the step chemical potential is obtained that contains two energetic contributions—one from the adjacent terraces in the form of the jump in the adatom grand canonical potential and the other from the monolayer of crystallized adatoms that underlies the upper terrace in the form of the nominal bulk chemical potential—thus generalizing the classical Gibbs-Thomson relation to the dynamic, dissipative setting of step-flow growth. The linear stability analysis of the resulting quasistatic free-boundary problem for an infinite train of equidistant rectilinear steps yields explicit—i.e., analytical—criteria for the onset of step bunching in terms of the basic physical and geometric parameters of the theory. It is found that, in contrast with the predictions of the classical BCF model, both in the absence as well as in the presence of desorption, a growth regime exists for which step bunching occurs, except possibly in the dilute limit where the train is always stable to step bunching. In the present framework, the onset of one-dimensional instabilities is directly attributed to the energetic influence on the migrating steps of the adjacent terraces. Hence the theory provides a "minimalist" alternative to existing theories of step bunching and should be relevant to, e.g., molecular beam epitaxy of GaAs where the equilibrium adatom density is shown by Tersoff, Johnson, and Orr [Phys. Rev. B **78**, 282 (1997)] to be extremely high.

DOI: 10.1103/PhysRevB.75.165409 PACS number(s): 81.10.Aj, 81.15.Aa, 81.15.Hi, 81.15.Kk

I. INTRODUCTION

At sufficiently high growth temperatures, thin-film epitaxy proceeds via the flow of steps on the vicinal surface that separates the crystalline phase from the vacuum or vapor [for an overview of molecular beam epitaxy (MBE), see Ref. 1; for a general introduction to crystal growth, see Refs. 2–4; for a comprehensive overview and discussion of step dynamics on vicinal surfaces, see Refs. 5 and 6]. Specifically, the adatom mobility is such that the nucleation and subsequent coalescence of monatomic islands can be reasonably ignored. Correspondingly, the growth results solely from the attachment and detachment of adatoms to the edges of preexisting steps and their subsequent incorporation into the crystalline phase. A proper accounting of step dynamics is thus fundamental to the understanding of the growth process. Of chief importance are one- and two-dimensional instabilities, bunching, and meandering, respectively, that alter the configuration and morphology of steps. Whereas step bunching refers to the formation of periodic arrays of rectilinear monatomic steps separated by wide terraces, meandering designates the waviness of individual steps that sometimes accompanies their migration, cf., e.g., Ref. 7. The stability analysis presented below, see Sec. IV, is concerned with step bunching, even though the general theory that we derive from the fundamental principles of continuum physics is two-dimensional, see Sec. III, and is hence appropriate for the investigation of step meandering.

By normal Ehrlich-Schwoebel barrier we mean an asymmetry in the attachment-detachment kinetics by which it is energetically more favorable for adatoms approaching a step from the lower adjacent terrace to attach to its edge than it is for those adatoms nearing the same step from the upper terrace. Within the setting of the classical Burton-Cabrera-Frank (BCF) theory,[8] it is well known that, in the absence of evaporation and in the presence of a normal Ehrlich-Schwoebel effect, a train of initially equidistant and straight steps remains so during growth, see Refs. 3, 9, and 10. Hence the classical BCF theory precludes step bunching during condensation. But there exists ample experimental evidence that such bunching of steps does occur during growth, see, e.g., the discussion of Krug,[5] and the references therein. Therefore, the classical BCF framework has had to be extended to permit such one-dimensional instabilities. In particular, the following augmented BCF-type theories have been proposed: impurity-based step bunching;[11] step bunching due to an inverse Ehrlich-Schwoebel effect, i.e., the preferential attachment of terrace adatoms to descending steps, see Ref. 12 and the discussion of Krug;[5] chemistry-driven step bunching in binary systems;[13–15] step bunching induced by electromigration;[16] step bunching due to fast edge diffusion;[17,18] or resulting from a strong anisotropy in the terrace-adatom diffusion;[19] etc.

In the present investigation, we propose a thermodynamically consistent, minimalist field theory for the step-flow epitaxy of single-species crystalline films. By minimalist, we mean a theory that does not account for the presence of advacancies and/or impurities, ignores edge atomic diffusion, is oblivious of possible anisotropies in the thermodynamic and kinetic properties of steps and terraces, and, being concerned with single-component crystals, makes no provision for chemical interactions between atoms of distinct species whose kinetics might otherwise impact on the surface morphology. By thermodynamically consistent, we mean a continuum framework guided by the second law, which, in isothermal settings such as ours, combines with the energy balance to yield a dissipation inequality that informs and imposes certain restrictions on the choice of energetic and kinetic parameters that enter the theory, cf., Eqs. (15), (16), (19), and (24) below. In particular, we arrive at an expression for the step chemical potential

$$\mu^s = \mu^b - \frac{[\![\omega]\!]}{a\varrho^b}, \tag{1}$$

which specializes to settings in which the step energetic structure can be ignored the more general relation for the step chemical potential derived in Ref. 20.

$$\mu^s = \mu^b - \frac{1}{a\varrho^b}\{[\![\omega]\!] + \tilde{\Psi}^s\kappa\}. \tag{2}$$

Equation (1), in turn, yields boundary conditions along the migrating steps, see Eqs. (4) and (5) below, that differ from those of the classical BCF theory (the compatibility of ours with the standard BCF model is briefly discussed at the end of Sec. III). Here, μ^b is the (nominal) crystalline chemical potential, a is the step height, ϱ^b is the bulk atomic density (per unit volume), $\tilde{\Psi}^s$ is the stiffness of the step and κ its curvature, and $[\![\omega]\!]$ is the jump in the terrace grand canonical potential across the step.

Most importantly, the linear stability analysis of the resulting free-boundary problem shows that, both in the absence as well as in the presence of adatom desorption, and assuming that the normal Ehrlich-Schwoebel effect is operative, a growth regime exists for which step bunching occurs, see Sec. IV for details. In short, the energetic contribution of the adjacent terraces to the step chemical potential—in the form of the jump in the grand canonical potential—provides a mechanism which, under certain growth conditions and for an appropriate choice of material parameters, triggers the kind of one-dimensional instabilities that are observed experimentally, see, e.g., Ref. 5. Interestingly, this energetic term is absent from the more standard BCF-type theories, with the notable exception of the variational calculation of Jeong and Williams,[6] and it therefore comes as no surprise that its potential role in the onset of step bunching has been altogether ignored. Finally, it is important to note that this energetic contribution is of significance only when the equilibrium adatom density ϱ_{eq} is of the same magnitude as the density of crystallized adatoms $a\varrho^b$. As discussed by Tersoff, Johnson, and Orr,[21] this is the case for GaAs surfaces equilibrated under conditions similar to those of MBE. Indeed, evidence, both theoretical and experimental, is presented in support of extremely high gallium-adatom densities and, subsequently, for near-equilibrium growth, see also Ref. 22. Further, it is conjectured that such unexpectedly high equilibrium adatom densities could characterize growth of other compound semiconductors (which can be treated as effective one-component systems thus fitting into the present single-species framwork). When $\varrho_{\mathrm{eq}} \ll a\varrho^b$, i.e., in the dilute limit, our analysis predicts that a train of equidistant, straight steps will be stable to step bunching during deposition, with or without evaporation.

In summary, for a single step separating two adjacent terraces, the terrace adatom density ϱ and step velocity V are solutions of the free-boundary problem consisting of the "hybrid" reaction-diffusion equation

$$\partial_t\varrho = M\Delta\mu + F - \sigma\mu, \tag{3}$$

on the upper and lower terraces, with μ the adatom chemical potential, M the atomic mobility, F the deposition flux, and σ the desorption coefficient, subject to the step-edge "flux-matching" boundary conditions

$$\begin{aligned} \varrho^+ V + M(\nabla\mu)^+ \cdot \mathbf{n} &= C_+(\mu^+ - \mu^s), \\ -\varrho^- V - M(\nabla\mu)^- \cdot \mathbf{n} &= C_-(\mu^- - \mu^s), \end{aligned} \tag{4}$$

along the step, with $\mathbf{n}$ the unit normal to the step pointing into the lower terrace, C_+ (C_-) the kinetic coefficient for the attachment-detachment of adatoms from the lower (upper) terrace onto the step edge, and, letting φ be a field defined on the terraces, φ^+ (φ^-) denotes the limiting value of φ as the step is approached from the lower (upper) terrace. Finally, Eqs. (3) and (4) are supplemented by the step atomic-density balance

$$a\varrho^b V = C_+(\mu^+ - \mu^s) + C_-(\mu^- - \mu^s), \tag{5}$$

with the step chemical potential satisfying Eq. (1) or, more generally, Eq. (2). In the absence of desorption, and assuming that the time scale for the migration of steps is slow in comparison with that which characterizes the diffusion of adatoms on the terraces, the linear stability analysis of the quasistatic version of the free-boundary problem (3)–(5) for an infinite periodic train of equidistant rectilinear steps whose period L equals the width of two adjacent terraces (see Sec. IV for details) yields the following stability criterion: A train of equidistant steps is stable with respect to step pairing if

$$0 \leqslant \Theta < \Theta_c = \frac{M(C_+ - C_-)}{2M(C_+ + C_-) + C_+C_-L}, \tag{6}$$

whereas the bunching of steps occurs for

$$\Theta_c < \Theta < \Theta_d = \frac{2M(C_+ + C_-) + C_+C_-L}{4M(C_+ - C_-)}, \tag{7}$$

with $\Theta := \frac{\varrho_{\mathrm{eq}}}{a\varrho^b}$ a dimensionless parameter that measures the equilibrium adatom density relative to the bulk atomic density (per unit area). In Sec. IV B, we also derive an explicit stability criterion for step-flow growth in the presence of desorption, see Eqs. (51)–(53).

The remainder of this article is organized as follows. In Sec. II, we briefly discuss the classical BCF model with the goal of contrasting the standard theory with the one derived herein. Section III is devoted to the derivation of a thermodynamically compatible, minimalist theory for the step-flow epitaxy of single-component crystalline films. This is followed in Sec. IV by a linear stability analysis of the resulting quasistatic free-boundary problem as it applies to an infinite train of rectilinear steps with and without desorption. In particular, analytical stability criteria are explicitly derived that characterize the onset of step bunching in terms of the physical and geometric parameters of the theory and, in the case of growth with desorption, our final results are illustrated in the morphological phase diagrams on display in Fig. 4. Section V concludes with a summary and a brief discussion of the relevance and limitations of the proposed theory.

II. THE CLASSICAL BCF MODEL

The simplest two-dimensional BCF model for single-species epitaxy (cf., e.g., Ref. 7) consists of steady-state reaction-diffusion equations on the terraces:

$$D\Delta\varrho + \bar{F} - \bar{\sigma}\varrho = 0, \tag{8}$$

supplemented by boundary conditions along the migrating step edges of the form

$$\begin{aligned} D(\nabla\varrho)^{+}\cdot\mathbf{n} &= \bar{K}_{+}(\varrho^{+} - \varrho_{\mathrm{eq}} - \Gamma\kappa), \\ -D(\nabla\varrho)^{-}\cdot\mathbf{n} &= \bar{K}_{-}(\varrho^{-} - \varrho_{\mathrm{eq}} - \Gamma\kappa), \end{aligned} \tag{9}$$

and augmented by evolution equations for the steps in the form of atomic-density balances

$$a\varrho^{b}V = D[\![\nabla\varrho]\!]\cdot\mathbf{n}. \tag{10}$$

Here, ϱ is the terrace adatom density and $\Delta\varrho$ its two-dimensional Laplacian, D is the atomic diffusion coefficient, $\bar{F}$ is the (constant) deposition flux, and $\bar{\sigma}$ the desorption coefficient; $\bar{K}_{+}$ ($\bar{K}_{-}$) is the adatom attachment-detachment coefficient from the lower (upper) adjacent terrace onto the step edge, $\mathbf{n}$ the unit normal to the step pointing into the lower terrace and κ its curvature, ϱ_{eq} the equilibrium adatom density when the steps are flat (i.e., for $\kappa=0$), Γ a constant parameter, and, for a given terrace field φ, φ^{+} (φ^{-}) denotes the limiting value of φ as the step is approached from the lower (upper) terrace; a is the lattice parameter along the growth direction, ϱ^{b} the bulk atomic density (per unit volume), V the step velocity, and $[\![\nabla\varrho]\!] := (\nabla\varrho)^{+} - (\nabla\varrho)^{-}$ is the jump in the adatom-density gradient across the step. (In Ref. 7, $\Gamma := \frac{\gamma}{\varrho^{b}k_{B}T}$, with γ the constant step line tension or, equivalently, the step free energy per unit length, k_B the Boltzmann constant, and T the fixed growth temperature.)

Underlying the free-boundary problem (8)–(10) is the tacit assumption that the motion of steps occurs on a time scale that is slow compared with that which characterizes adatom diffusion on the terraces, an assumption upon which our linear stability analysis is also based. Hence the transient term $\partial_t\varrho$ is neglected on the right-hand side of Eq. (8), as are the "convective" adatom inflows from the adjacent terraces into the steps $\varrho^{+}V$, $-\varrho^{-}V$, and $-[\![\varrho]\!]V$, on the left-hand sides of Eqs. (9) and (10), respectively. Further, adatom terrace diffusion is assumed isotropic and, in the same vein, the dependence of the step free-energy density and attachment-detachment coefficients on its orientation is ignored. Finally, the classical BCF theory is oblivious of edge diffusion and, although endowed with an energetic structure, the steps are assumed unable to sustain mass. (Herein, we too will ignore edge diffusion and neglect the density of adatoms along the steps; for a more general theory, see, e.g., Ref. 20.)

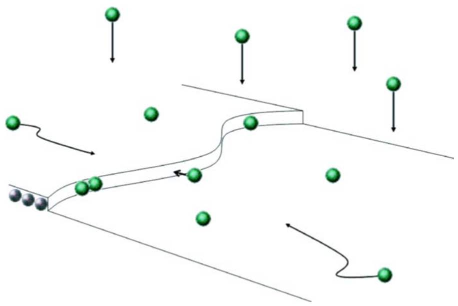

FIG. 1. (Color online) Three-dimensional schematic of a single monatomic step separating two adjacent terraces upon which adsorption-desorption occurs, accompanied by adatom diffusion.

In what follows, we generalize the classical BCF theory, obtaining step evolution equations that differ from Eqs. (9) and (10). We then show that these non-classical boundary conditions provide the basis for a distinct step-bunching instability.

III. BEYOND THE CLASSICAL BCF THEORY: A THERMODYNAMICALLY CONSISTENT MODEL

Consider a single monatomic step separating two adjacent terraces (see Fig. 1). Let $\mathcal{S}=\mathcal{S}(t)$, a smooth, time-dependent, simple curve in $\mathbb{R}^2$, be the projection of the step onto the plane, and denote by $\Omega_{+}=\Omega_{+}(t)$ and $\Omega_{-}=\Omega_{-}(t)$, both time dependent, open domains in $\mathbb{R}^2$, the projections of the lower and upper terraces respectively (see Fig. 2). Away from the step, the adatom density balance reduces to

$$\partial_t\varrho = -\operatorname{div}\mathbf{h} + R \quad \text{on } \Omega_{+}\cup\Omega_{-}, \tag{11}$$

with $\mathbf{h}$ the adatom diffusive flux, $\operatorname{div}\mathbf{h}$ its two-dimensional divergence, and R the atomic supply to the terraces from the adjacent vacuum or vapor. Along the step $\mathcal{S}$, the adatom density balance yields the jump conditions

$$\begin{aligned} J_{+} &= \varrho^{+}V - \mathbf{h}^{+}\cdot\mathbf{n}, \\ -J_{-} &= \varrho^{-}V - \mathbf{h}^{-}\cdot\mathbf{n}, \end{aligned} \tag{12}$$

where J_{+} (J_{-}) is the scalar influx of adatoms from the lower (upper) terrace Ω_{+} (Ω_{-}) into the step edge and V is the step

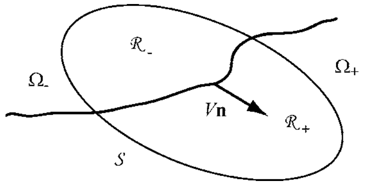

FIG. 2. A monatomic step idealized as a smoothly evolving curve $\mathcal{S}=\mathcal{S}(t)$ in the plane, separating the trace of the lower terrace Ω_{+} from its upper counterpart Ω_{-}. Here, the step velocity is assumed purely normal, $\mathbf{v}=V\mathbf{n}$, and $\mathcal{R}_{+}$ ($\mathcal{R}_{-}$) is the intersection of the lower (upper) terrace with an arbitrary two-dimensional domain $\mathcal{R}$.

intrinsic velocity. Finally, accounting not only for the terrace adatoms but also for their crystallized counterparts, i.e., adatoms that have already been incorporated into the bulk layer underlying the upper terrace, the atomic-density balance yields the step evolution equation[20]

$$a\varrho^b V = J_+ + J_- \quad \text{along } \mathcal{S}. \tag{13}$$

Constitutive prescriptions for $\mathbf{h}$, R, J_+, and J_- should be consistent with the second law which, in an isothermal setting such as that which characterizes epitaxial growth at fixed temperature, combines with the energy balance into a single inequality. This so-called dissipation inequality states that the rate at which the energy associated with an arbitrary two-dimensional domain $\mathcal{R}$ increases is bounded by the rate at which energy is transported via diffusion across its boundary $\partial\mathcal{R}$ augmented by the rate at which energy is supplied by condensation evaporation onto $\mathcal{R}$:

$$\underbrace{\frac{d}{dt}\left(\int_{\mathcal{R}}\Psi da + \int_{\mathcal{R}_-} a\Psi^b da\right)}_{\text{total free energy contained in } \mathcal{R}} \leqslant \underbrace{-\int_{\partial\mathcal{R}} \mu\mathbf{h}\cdot\mathbf{n}_{\partial\mathcal{R}} ds}_{\text{energy inflow via adatom diffusion}} + \underbrace{\int_{\mathcal{R}} \mu^v R da}_{\text{energy intake through adsorption-desorption}}, \tag{14}$$

where $\mathcal{R}_- := \mathcal{R}\cap\Omega_-$ ($\mathcal{R}_+ := \mathcal{R}\cap\Omega_+$) is the section of $\mathcal{R}$ that fall within the upper (lower) terrace and $\mathbf{n}_{\partial\mathcal{R}}$ is the outer unit normal to the boundary of $\mathcal{R}$ (see Fig. 2), Ψ is the terrace free-energy density (per unit area), Ψ^b the free-energy density (per unit volume) associated with the crystallized atoms within the bulk monolayer immediately underlying the upper terrace, μ is the adatom chemical potential, and μ^v its vapor or beam counterpart. (Note that the adatom chemical potential μ is viewed herein as a primitive field, the energy per unit transported mass on the terraces. A similar remark holds for the vapor chemical potential μ^v defined as the energy per unit exchanged mass between surface and vapor/beam.) Appealing to Eq. (11), localization of Eq. (14) away from the step yields the pointwise inequality

$$\partial_t\Psi - \mu\partial_t\varrho + \mathbf{h}\cdot\nabla\mu - (\mu^v - \mu)R \leqslant 0 \quad \text{on } \Omega_+\cup\Omega_-, \tag{15}$$

whereas, by Eqs. (12) and (13), localization of Eq. (14) along the step takes the form

$$\left\{\mu^- - \frac{\Psi^b}{\varrho^b} + \frac{[\![\omega]\!]}{a\varrho^b}\right\}J_- + \left\{\mu^+ - \frac{\Psi^b}{\varrho^b} + \frac{[\![\omega]\!]}{a\varrho^b}\right\}J_+ \geqslant 0, \tag{16}$$

where

$$\omega := \Psi - \mu\varrho$$

is the adatom grand canonical potential (per unit area).

We let $\Psi = \Psi(\varrho)$ and choose $\mathbf{h}$ and $\mathbf{R}$ such that

$$\mathbf{h} = -M\nabla\mu,$$

$$\mathbf{R} = -\sigma(\mu - \mu^v), \tag{17}$$

with the adatom mobility M and the evaporation-condensation coefficient σ non-negative constants. A standard extension of a variational procedure first introduced by Coleman and Noll[23] (see also Refs. 24–27) yields:

$$\mu = \partial_\varrho\Psi, \tag{18}$$

and the dissipation inequality (15) reduces to

$$\Pi_{\text{terr}} := -\mathbf{h}\cdot\nabla\mu - (\mu^v - \mu)R = M|\nabla\mu|^2 + \sigma(\mu - \mu^v)^2 \geqslant 0, \tag{19}$$

with Π_{terr} the dissipation per unit area due to terrace adatom diffusion and adsorption-desorption kinetics. If the terrace adatoms behave collectively like a binary regular solution, its two contituents being the adatoms and the open adsorption sites, then, letting ϵ denote the bond strength per adatom, we have (see, e.g., Ref. 1)

$$\Psi = \underbrace{4a\epsilon\varrho^b x(1-x)}_{\text{internal energy}} + \underbrace{a\varrho^b k_B T\{x\ln x + (1-x)\ln(1-x)\}}_{-T\times(\text{entropy of mixing})}, \tag{20}$$

where k_B is the Boltzmann constant, T the fixed growth temperature, and x, the adatom coverage, is defined by $x := \frac{\varrho}{a\varrho^b}$. By Eq. (18), it follows that

$$\mu = 4\epsilon(1-2x) + k_B T \ln\left\{\frac{x}{1-x}\right\}. \tag{21}$$

Finally, the simplest constitutive prescriptions for J_+ and J_- consistent with the dissipation inequality along the step (16) are given by:

$$J_+ = C_+(\mu^+ - \mu^s),$$

$$J_- = C_-(\mu^- - \mu^s), \tag{22}$$

where C_+ and C_- are constant, non-negative, attachment-detachment coefficients, and μ^s, interpreted as the step chemical potential, is prescribed according to

$$\mu^s := \frac{\Psi^b}{\varrho^b} - \frac{[\![\omega]\!]}{a\varrho^b}. \tag{23}$$

It follows from Eq. (22) that the step dissipation inequality (16) reduces to

$$\begin{aligned}\Pi_{\text{step}} &:= (\mu^- - \mu^s)J_- + (\mu^+ - \mu^s)J_+ \\ &= C_-(\mu^- - \mu^s)^2 + C_+(\mu^+ - \mu^s)^2 \geqslant 0,\end{aligned} \tag{24}$$

with μ^s specified by Eq. (23) and Π_{step} the dissipation (per unit length) along the step due solely to adatom attachment-detachment kinetics. That the right-hand side of Eq. (23) should be interpreted as the step chemical potential is discussed at length in Cermelli and Jabbour,[20] where, in the presence of edge diffusion, μ^s, defined as the energy per unit transported mass along the steps, enters the theory in a most natural way.

In summary, the adatom density and step velocity are solutions of the free-boundary problem consisting of the reaction-diffusion equation on the upper and lower terraces:

$$\partial_t\varrho = M\Delta\mu + F - \sigma\mu, \tag{25}$$

with $F := \sigma\mu^v$, subject to the step-edge boundary conditions

$$\varrho^{+}V + M(\boldsymbol{\nabla}\mu)^{+}\cdot\mathbf{n} = C_{+}(\mu^{+}-\mu^{s}),$$

$$\varrho^{-}V + M(\boldsymbol{\nabla}\mu)^{-}\cdot\mathbf{n} = -C_{-}(\mu^{-}-\mu^{s}), \qquad (26)$$

and the step evolution equation

$$a\varrho^{b}V = C_{+}(\mu^{+}-\mu^{s}) + C_{-}(\mu^{-}-\mu^{s}), \qquad (27)$$

where the step chemical potential is given by

$$\mu^{s} = \mu^{b} - \frac{1}{a\varrho^{b}}[\![\omega]\!], \qquad (28)$$

with $\mu^{b} := \frac{\Psi^{b}}{\varrho^{b}}$ the nominal bulk chemical potential.

As for the consistency of the classical BCF model, see Eqs. (8)–(10), with the generalized theory, see Eqs. (25)–(27) or, equivalently, the compatibility of the classical BCF equations with the second law, we proceed as follows. Let ϱ_{eq} denote the equilibrium adatom density. A trivial exercise shows that the classical reaction-diffusion equation (8) is a first-order approximation of Eq. (25) about the equilibrium state provided that $D = M\mu'(\varrho_{\mathrm{eq}})$, $\bar{\sigma} = \sigma\mu'(\varrho_{\mathrm{eq}})$, and $\bar{F} = F - \sigma\mu(\varrho_{\mathrm{eq}}) + \sigma\mu'(\varrho_{\mathrm{eq}})\varrho_{\mathrm{eq}}$. These rescalings also ensure that the step atomic-density balance (27) can be approximated to first order in ϱ by the classical step evolution equation (10). As for the compatibility of the step boundary conditions (26) with their classical counterparts (9), it can easily be shown that, in the limit $\varrho_{\mathrm{eq}} \ll a\varrho^{b}$, i.e., when the equilibrium adatom density is negligible relative to its bulk counterpart (per unit area), the former conditions can be approximated by the latter conditions to first order in ϱ, granted that $\bar{K}_{\pm} = C_{\pm}\mu'(\varrho_{\mathrm{eq}})$.[20] It can thus be concluded that the classical free-boundary problem (8)–(10) constitutes a first-order approximation of its thermodynamically consistent counterpart (25)–(27) in the dilute limit and for small departures from equilibrium. Importantly, when ϱ_{eq} is of the same order as $a\varrho^{b}$, as in the case of GaAs growth,[21] the classical BCF model may no longer be valid insofar as the edge boundary conditions (26) should replace Eq.(9).

IV. STABILITY ANALYSIS FOR A TRAIN OF EQUIDISTANT STEPS

When the time scale for the migration of steps is large compared to the time scale for the diffusion of adatoms on the terraces, the reaction-diffusion equation (25) is approximated by its steady-state counterpart

$$M\Delta\mu + F - \sigma\mu = 0 \qquad (29)$$

on the terraces, and the boundary conditions (26) are replaced by

$$M(\partial_{n}\mu)^{+} = C_{+}(\mu^{+}-\mu^{s}),$$

$$-M(\partial_{n}\mu)^{-} = C_{-}(\mu^{-}-\mu^{s}), \qquad (30)$$

along the step edges, with $\partial_{n}\mu := \boldsymbol{\nabla}\mu\cdot\mathbf{n}$ the normal derivative of the step chemical potential, while Eqs. (27) and (28) remain unchanged. Hence the free-boundary problem (29) and (30) is now formulated exclusively in terms of the adatom chemical potential and decouples from the step evolution equation (27) by which the step velocity is determined.

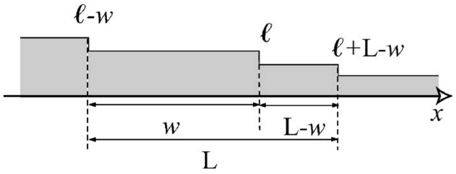

FIG. 3. One-dimensional schematic view of a section of a two-terrace periodic array of parallel rectilinear steps.

A. Step flow without desorption

Consider an infinite array of parallel rectilinear steps, choose coordinates (x,y) with the y axis parallel to the steps, and assume that all fields are independent of y. Under these assumptions the problem becomes one dimensional. Moreover, let $l_i(t)$ be the trace of the ith step along the x axis (i integer), and assume that $l_{i+2}(t) = l_i(t) + L$ for each i, with $L > 0$ fixed (see Fig. 3). Finally, denote by $\mu_i = \mu_i(x,t)$ the adatom chemical potential on the terrace $[l_i, l_{i+1}]$.

Assume now that the adatom chemical potential is such that $\partial_{\varrho}\mu \neq 0$. [If the terrace adatoms are idealized as a binary regular solution whose other constituent is the "species" of open adsorption sites, see Eq. (20), then, by Eq. (21), it follows that $\partial_{\varrho}\mu = \frac{1}{a\varrho^{b}}\left\{-8\epsilon + \frac{k_B T}{x(1-x)}\right\}$. Hence, if the bond energy per adatom satisfies $\epsilon < \frac{1}{2}k_B T$, the terrace chemical potential μ is an invertible function of the adatom density ϱ since $\partial_{\varrho}\mu > 0$ for all $x \in (0,1)$ or, equivalently, for all $\varrho \in (0, a\varrho^{b})$. If the growth temperature is chosen such that $T = \frac{2\epsilon}{k_B}$, the adatom chemical potential μ is invertible for $x \in \left(0, \frac{1}{2}\right)$ or $x \in \left(\frac{1}{2}, 1\right)$. Finally, if $T < \frac{2\epsilon}{k_B}$, $\partial_{\varrho}\mu = 0$ for $x = x_{1,2} = \frac{1}{2} \pm \frac{1}{2}\left(1 - \frac{k_B T}{2\epsilon}\right)^{1/2}$, and the chemical potential is invertible for values of ϱ in $(0, a\varrho^{b}x_2)$ or $(a\varrho^{b}x_2, a\varrho^{b}x_1)$ or $(a\varrho^{b}x_1, a\varrho^{b})$. It is thus clear that adatom-concentration intervals exist for which the chemical potential is an invertible function of the adatom density irrespective of the growth temperature.] Hence μ is an invertible function of the adatom density, and it follows that the adatom grand canonical potential can be expressed as a function of μ. Expanding about μ_{eq} and truncating terms higher than the first order, we have the linear approximation

$$\omega \approx \omega_0 - \varrho_{\mathrm{eq}}\mu \qquad (31)$$

for the terrace grand canonical potential, with $\varrho_{\mathrm{eq}} := \mu^{-1}(\mu_{\mathrm{eq}})$ and $\omega_0 := \omega(\mu_{\mathrm{eq}}) + \varrho_{\mathrm{eq}}\mu_{\mathrm{eq}}$ positive constants. [Note that, appealing to the definition of the grand canonical potential and the relation (18), we have $\partial_{\varrho}\omega = -\varrho\partial_{\varrho}\mu$. Hence, by the chain rule, $\partial_{\mu}\omega = -\varrho$.]

For simplicity, we now formally assume that $\sigma = 0$, i.e., we ignore adatom desorption. Hence, Eq. (29) reduces to the steady-state diffusion equation on the terraces and, together with the flux-matching boundary conditions (30) along the steps, yields the boundary-value problem

$$M\partial^{2}_{xx}\mu_i + F = 0, \qquad (32)$$

for $x \in [l_i(t), l_{i+1}(t)]$, and

$$M\partial_x\mu_i = C_+\{\mu_i - \mu^b - \Theta(\mu_i - \mu_{i-1})\},$$

$$-M\partial_x\mu_i = C_-\{\mu_i - \mu^b - \Theta(\mu_{i+1} - \mu_i)\}, \qquad (33)$$

at $x = l_i(t)$ and $x = l_{i+1}(t)$, respectively, where

$$\Theta := \frac{\varrho_{\rm eq}}{a\varrho^b}$$

measures the equilibrium adatom density relative to the density of crystallized atoms (per unit area). Furthermore, we consider periodic solutions of Eq. (32), i.e., we confine the analysis to solutions that satisfy $\mu_i(x,t) = \mu_{i+2}(x+L,t)$. Hence, it is sufficient to study the evolution of two adjacent terraces, say, those bounded by the steps

$$l_0 = l - w, \quad l_1 = l, \quad l_2 = l + L - w,$$

so that w is the width of the terrace $[l_0, l_1]$ and $L - w$ is the width of the terrace $[l_1, l_2]$ (see Fig. 3).

We now derive an evolution equation for w. Note first that the solution of Eq. (32) on the terraces $[l - w, l]$ and $[l, l + L - w]$ is of the form

$$\mu_0 = -\frac{F}{2M}(x - l + w)^2 + c_1(x - l + w) + c_2,$$

$$\mu_1 = -\frac{F}{2M}(x - l)^2 + c_3(x - l) + c_4, \qquad (34)$$

for $x \in [l - w, l]$ and $x \in [l, l + L - w]$, respectively, where the coefficients $c_i = c_i(w)$ $(1 \leqslant i \leqslant 4)$ depend on the width w of the terrace $[l_0, l_1]$, on the step attachment-detachment kinetic coefficients C_+ and C_-, on the atomic mobility M, on the deposition flux F, and on the parameters Θ and L. [The functions $c_i(w)$ are determined explicitly by inserting Eq. (34) into Eq. (33) and solving the resulting linear system. Here, for the purpose of conciseness, we have omitted such explicit expressions.] Next, the atomic-density balance (13) provides two evolution equations for the steps $l_0 = l - w$ and $l_1 = l$. Specifically, making use of the two-terrace periodicity, Eq. (13) yields

$$a\varrho^b(\dot{l} - \dot{w}) = J_0^+ + J_1^-,$$

$$a\varrho^b\dot{l} = J_1^+ + J_0^-, \qquad (35)$$

with J_0^+ (J_1^+) and J_0^- (J_1^-) the attachment fluxes of adatoms from the terrace $[l - w, l]$ ($[l, l + L - w]$) onto the edges of its upper and lower bounding steps l_0 (l_1) and l_1 (l_2), respectively. Subtracting the second expression of Eq. (35) from the first, we arrive at

$$a\varrho^b\dot{w} = J_1^+ + J_0^- - J_0^+ - J_1^-. \qquad (36)$$

Finally, upon substitution of Eq. (34) into Eq. (36), we obtain the evolution equation for the width w:

$$a\varrho^b\dot{w} = f(w) := \frac{FM(C_+ + C_-)(A - \Theta B)}{C(w) - \Theta AB}(L - 2w), \qquad (37)$$

where $A := M(C_+ - C_-)$, $B := 2M(C_+ + C_-) + LC_+C_-$, and $C(w) := \{M(C_+ + C_-) + C_+C_-w\}\{M(C_+ + C_-) + C_+C_-(L - w)\}$.

By Eq. (37), one trivially concludes that $f(L/2) = 0$, so that a train of equidistant steps moving with constant velocity is a solution of Eq. (32). Importantly, this solution is stable if $f'(L/2) < 0$. Given that

$$f'(L/2) = -\frac{8FM(C_+ + C_-)(A - \Theta B)}{B(B - 4\Theta A)}, \qquad (38)$$

with A and B prescribed as above, it follows that in the absence of desorption, a two-terrace periodic train of equidistant rectilinear steps is stable with respect to bunching if

$$0 \leqslant \Theta < \Theta_c := \frac{M(C_+ - C_-)}{2M(C_+ + C_-) + C_+C_-L}, \qquad (39)$$

whereas the bunching of steps occurs for

$$\Theta_c < \Theta < \Theta_d := \frac{2M(C_+ + C_-) + C_+C_-L}{4M(C_+ - C_-)}, \qquad (40)$$

since for $\Theta = \Theta_d$ the denominator of Eq. (38) changes sign. (Note that $\Theta_d = \frac{1}{4\Theta_c}$, from which it follows that $\Theta_c < \frac{1}{2}$. Appealing to Eq. (39), the latter necessary condition is tantamount to $4MC_- + C_+C_-L > 0$ and is hence trivially satisfied.)

B. Step flow in the presence of desorption

When desorption is accounted for, the stationary diffusion equation (32) is replaced by the steady-state reaction-diffusion equation

$$M\partial^2_{xx}\mu_i - \tau^2\mu_i + F = 0, \quad x \in [l_i(t), l_{i+1}(t)], \qquad (41)$$

where, for convenience, we now refer to σ, the desorption coefficient, as τ^2. The resulting boundary-value problem, Eqs. (41) and (33), can be simplified by a suitable rescaling. Letting

$$\Phi := \frac{F}{\tau^2} - \mu^b, \quad \nu := \mu - \mu^b,$$

and introducing the dimensionless attachment-detachment kinetic coefficients

$$K_\pm := \frac{C_\pm}{\tau\sqrt{M}},$$

and the dimensionless lengths

$$\xi := \frac{\tau x}{\sqrt{M}}, \quad \Lambda := \frac{\tau L}{\sqrt{M}}, \quad \zeta := \frac{\tau w}{\sqrt{M}}, \quad \lambda_i := \frac{\tau l_i}{\sqrt{M}},$$

we can rewrite Eqs. (41) and (33) in the form

$$\partial^2_{\xi\xi}\nu_i - \nu_i + \Phi = 0, \qquad (42)$$

for $\xi \in [\lambda_i(t), \lambda_{i+1}(t)]$, and

$$\partial_\xi\nu_i = K_+\{(1 - \Theta)\nu_i + \Theta\nu_{i-1}\},$$

$$-\partial_\xi\nu_i = K_-\{(1 + \Theta)\nu_i - \Theta\nu_{i+1}\}, \qquad (43)$$

at $\xi = \lambda_i(t)$ and $\xi = \lambda_{i+1}(t)$, respectively. Repeating the same procedure as in Sec. IV A (but omitting the details), we arrive at the evolution equation for the rescaled width ζ:

$$a\varrho^b\dot{\zeta} = g(\zeta) := \frac{N(\zeta)}{D(\zeta)}, \tag{44}$$

where $N(\zeta)$ and $D(\zeta)$ are given by

$$N(\zeta) := \beta\Phi\{(\delta-\Theta\beta)\sinh(\Lambda-2\zeta)+\Theta\beta[\sinh\zeta-\sinh(\Lambda-\zeta)]+2\Theta(\alpha-1)[\cosh\zeta-\cosh(\Lambda-\zeta)]\}$$

and

$$D(\zeta) := \frac{1}{2}(\beta^2-\alpha^2-2\delta\beta\Theta+\beta^2\Theta^2)\cosh(\Lambda-2\zeta) + \frac{1}{2}(\alpha^2+\beta^2-2\delta\beta\Theta+\delta^2\Theta^2)\cosh\Lambda + \alpha(\beta-\Theta\delta)\sinh\Lambda-(\beta^2+\delta^2),$$

with

$$\alpha := 1+K_+K_-, \quad \beta := K_++K_-, \quad \delta := K_+-K_-. \tag{45}$$

[Note that $\alpha=1+\frac{1}{4}(\beta^2-\delta^2)$.]

As before, since $g(\Lambda/2)=0$, we conclude that a train of equidistant steps moving with constant velocity is a solution of Eq. (45). Further, this solution is stable if

$$g'(\Lambda/2) = \frac{N'(\Lambda/2)}{D(\Lambda/2)} < 0. \tag{46}$$

Now, fix Φ, Λ, α, β, and δ such that both Φ and δ are positive, i.e., the deposition flux F exceeds a critical value $F_c=\tau^2\mu^b$ and the asymmetry of the attachment-detachment coefficients is such that $K_+>K_-$. It is easily shown that $N'(\Lambda/2)$ vanishes for

$$\Theta_c := \frac{\delta}{\beta\left\{\cosh\dfrac{\Lambda}{2}+1\right\}+2(\alpha-1)\sinh\dfrac{\Lambda}{2}}, \tag{47}$$

whereas $D(\Lambda/2)=0$ for

$$\Theta_d := \frac{\{\exp\Lambda+1-2\exp(\Lambda/2)\}\{(\alpha+\beta)\exp\Lambda-\alpha+\beta\}}{\delta(\exp\Lambda-1)^2}. \tag{48}$$

Furthermore, $N'(\Lambda/2)$ is negative for $\Theta<\Theta_c$ and positive for $\Theta>\Theta_c$, while $D(\Lambda/2)$ is positive for $\Theta<\Theta_d$.

Finally, we prove that, for every Λ, β, and δ positive, $\Theta_c<\Theta_d$. Indeed, upon substitution of $\varsigma:=\exp(\Lambda/2)$ into Eqs. (47) and (48), we have

$$\Theta_c = \frac{2\delta}{(\beta+2\alpha-2)\varsigma^2+2\beta\varsigma-2\alpha+\beta+2}. \tag{49}$$

and

$$\Theta_d = \frac{(\alpha+\beta)\varsigma^2-\alpha+\beta}{\delta(\varsigma+1)^2}. \tag{50}$$

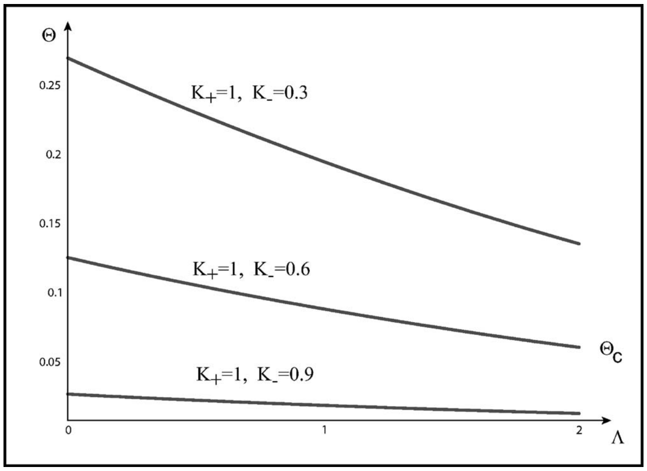

FIG. 4. The critical value Θ_c of $\Theta=\frac{\varrho_{\mathrm{eq}}}{a\varrho^b}$, beyond which step pairing occurs, as a function of the dimensionless period Λ for fixed K_+ and varying K_-. Note that Θ_c increases with $\delta=K_+-K_-=\frac{1}{\tau\sqrt{M}}(C_+-C_-)$, i.e., the barrier for the onset of step bunching is higher the more pronounced the normal Ehrlich-Schwoebel effect is.

Hence, for $\varsigma=1$ (i.e., when $\Lambda=0$), $\Theta_c=\frac{\delta}{2\beta}$ and $\Theta_d=\frac{\beta}{2\delta}$, so that, since $\delta<\beta$, $\Theta_c<\Theta_d$. Moreover, for every fixed β and δ, Θ_d is a positive, increasing function of ς for $\varsigma>1$, while Θ_c is positive and decreasing with respect to ς for $\varsigma>1$. Thus, for every β, δ and ς, $\Theta_c<\Theta_d$.

It follows that the critical surface $\Theta=\Theta_c(\Lambda,\beta,\delta)$ is contained in the region of the four-dimensional space of parameters $(\Theta,\Lambda,\beta,\delta)$ in which $D(\Lambda/2)$ is positive, and we conclude that $g'(\Lambda/2)<0$ for $0\leqslant\Theta<\Theta_c$, whereas $g'(\Lambda/2)>0$ for $\Theta_c<\Theta<\Theta_d$ (see Fig. 4). In summary, we have shown the following:

Provided that $\Phi=\frac{F}{\tau^2}-\mu^b>0$, a train of equidistant steps is stable with respect to step bunching if

$$0 \leqslant \Theta < \Theta_c \tag{51}$$

with

$$\Theta_c := \frac{C_+-C_-}{(C_++C_-)\left\{\cosh\dfrac{\tau L}{2\sqrt{M}}+1\right\}+\dfrac{2C_+C_-}{\tau\sqrt{M}}\sinh\dfrac{\tau L}{2\sqrt{M}}}. \tag{52}$$

Furthermore, the bunching of steps occurs when

$$\Theta_c < \Theta < \Theta_d, \tag{53}$$

where

$$\Theta_d := \frac{(\tau\sqrt{M} + C_+C_-)\left(\exp\frac{\tau L}{\sqrt{M}} - 1\right)}{(C_+ - C_-)\left(\exp\frac{\tau L}{2\sqrt{M}} + 1\right)^2} + \frac{(C_+ + C_-)}{(C_+ - C_-)\left(\exp\frac{\tau L}{2\sqrt{M}} + 1\right)}. \tag{54}$$

Finally, note that the above linear stability analysis should be confined to time scales comparable to that which characterizes the first coalescence of monatomic steps. As soon as the pairing of monatomic steps occurs, a new formalism is needed at least insofar as the adatom attachment-detachment kinetics and edge diffusion are expected to be different along biatomic steps than along monatomic ones. Hence, the dynamics of steps beyond first coalescence is not discussed herein. Nevertheless, we conjecture that a growth regime exists for which step pairs are unstable to bunching, with criteria for the onset of one-dimensional instabilities analogous to Eqs. (39) and (40) or (51)–(54). Similar remarks are in order for step quadruplets, i.e., pairs of monatomic-step pairs, step octuplets, etc.[3]

V. SUMMARY AND DISCUSSION

We have derived a thermodynamically compatible field theory for the epitaxial growth of single-species crytalline films. Two aspects of the proposed model are of chief importance. The first concerns the derivation of an expression for the step chemical potential, see Eq. (23) above, whose generalization to the case where the step is endowed with an orientation-dependent energy is given by[20]

$$\mu^s = \mu^b - \frac{1}{a\varrho^b}\{[\![\omega]\!] + \tilde{\Psi}^s\kappa\}. \tag{55}$$

The third term on the right-hand side of Eq. (55), $-\frac{1}{a\varrho^b}\tilde{\Psi}^s\kappa$, corresponds to the standard expression obtained by defining the step chemical potential as the variational derivative of the anisotropic free energy of a single step,[5] whereas the second term $-\frac{1}{a\varrho^b}[\![\omega]\!]$ results from redefining the step chemical potential as the variational derivative of a Hamiltonian that incorporates in some effective fashion step-step interactions.[6] Finally, the presence of the bulk chemical potential μ^b on the right-hand side of Eq. (55) results from a proper accounting of the influence of the monolayers of crystallized adatoms on the descending steps, see Eq. (14). This last term is absent from the more standard variational calculations, since the latter are oblivious of bulk-step interactions. In addition, whereas the variational treatment that yields Eq. (55), modulo the bulk chemical potential, is contingent on the geometric assumption that steps have weak curvature and on the physical approximation that nearest-neighbor effects are sufficient to describe step-step interactions, see Ref. 6, pp. 227, 228, the derivation of Cermelli and Jabbour[20] holds irrespective of such restrictions and is applicable in a broad sense to the dynamic, dissipative setting of step flow.

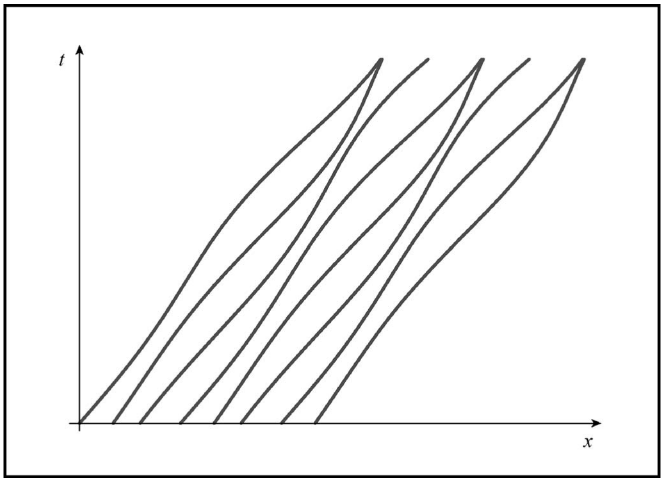

FIG. 5. One-dimensional simulation of the evolution of a three-periodic train of steps without desorption, Eq. (37), with $L=1$, $C_+=1$, $C_-=0.8$, $F=0.1$, $M=2$, $a\varrho^b=0.1$, and $\Theta=0.15$. The initial configuration corresponds to three nonequidistant steps per unit length, extended by periodicity outside the unit interval. Here $\Theta>\Theta_c=0.05$ and step pairing occurs in finite time.

The second main feature of our theory concerns the existence of a growth regime during which step-bunching instabilities occur (see Figs. 5 and 6). Indeed, Eq. (28) yields boundary conditions at the steps that differ from their counterparts upon which the more classical BCF-type theories are built, see Eqs. (26) and (27). Assuming that the equilibrium adatom coverage is sufficiently high—e.g., during the MBE growth of GaAs as discussed in Ref. 21—the stability analysis of the ensuing linearized (in the adatom chemical potential), quasistatic free-boundary problem yields analytical criteria for the onset of step bunching even under the assumption that the normal Ehrlich-Schwoebel barrier is operative, see Eqs. (39) and (40) for the case without desorption and Eqs. (51)–(54) for the case with desorption. This seems to be in contrast with the predictions of the classical

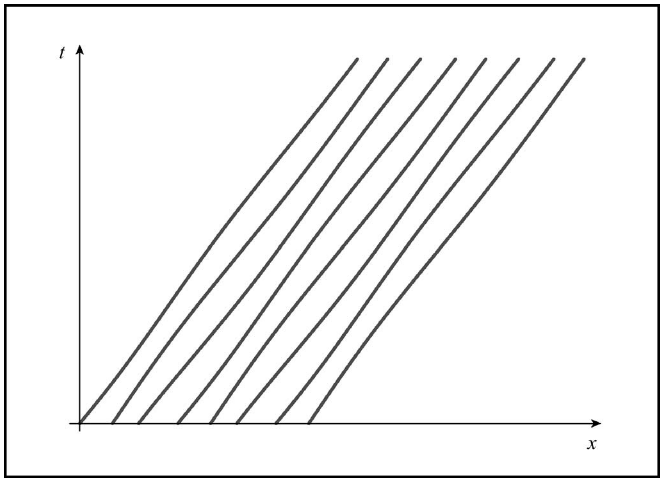

FIG. 6. One-dimensional simulation of the evolution of a three-periodic train of steps without desorption, see Eq. (37). The parameter values and initial conditions are as in Fig. 5. Here $\Theta=0.03<\Theta_c=0.05$ and the steps tend to become equidistant in finite time.

BCF model.[5,10] Indeed, a formal interpretation of the classical BCF-type analysis relates the stabilization of a configuration of equidistant, rectilinear steps by the normal Ehrlich-Schwoebel barrier to an effective step-step repulsion which is mediated by the diffusion of terrace adatoms. It could then be that a growth regime exists such that the energetic contribution of the adjacent terraces to the step chemical potential in the form of the jump in the grand canonical potential weakens this step-step repulsive interaction to the extent that its stabilizing effect is lost. Importantly, as discussed in Sec. I above, this thermodynamic effect is "intrinsic" to the most minimal BCF-type setting, i.e., the manifestation of step-bunching instabilities is not contingent on the presence of impurities (real or effective),[11] does not require chemical interactions between adatoms of distinct deposited species,[13] ignores contributions resulting from electromigration,[16] or due to edge diffusion,[17] is oblivious of anisotropy-driven effects,[19] and does not rely on the postulate of an inverse Ehrlich-Schwoebel barrier. Of course, ours is a highly idealized theory of step flow, precisely in that it ignores crystalline anisotropies in the energetic and kinetic properties of both terraces and steps and is oblivious of edge diffusion, etc. Hence validation via direct comparison with experimental data from step-flow growth on real vicinal surfaces might be of an elusive nature. Nevertheless, by delineating the thermodynamic influence of the adjacent terraces on the evolution of steps, we have put in evidence an alternative mechanism for the onset of one-dimensional instabilities, a mechanism which is operative even in the most minimalist of frameworks. The interplay between this energetic effect and other mechanisms underlying epitaxy—e.g., chemical interactions, anisotropy, edge diffusion, electromigration—will be the object of future investigations.

ACKNOWLEDGMENTS

The authors thank J. Krug for insightful discussions and for bringing to their attention the work of Tersoff, Johnson, and Orr. They also thank D. Margetis for his valuable comments. M.E.J. was supported by the NSF under Grant No. DMS-0605309 and by the KSEF under Grant No. KSEF-801-RDE-007. P.C. was supported by the Italian MIUR Research Grant 2005 "Modelli matematici per la scienza dei materiali."

---

*Electronic address: paolo.cermelli@unito.it
†Electronic address: jabbour@ms.uky.edu

[1] J. F. Tsao, *Materials Fundamentals of Molecular Beam Epitaxy* (Academic Press, New York, 1993).

[2] Y. Saito, *Statistical Physics of Crystal Growth* (World Scientific, Singapore, 1996).

[3] A. Pimpinelli and J. Villain, *Physics of Crystal Growth* (Cambridge University Press, Cambridge, 1998).

[4] J. P. V. der Eerden, in *Handbook of Crystal Growth*, edited by D. T. J. Hurle (North-Holland, Amsterdam, 1993), Vol. 1, Chap. 6, pp. 311–475.

[5] J. Krug, in *Multiscale Modeling in Epitaxial Growth*, edited by A. Voigt (Birkhauser, Berlin, 2005), Chap. 2, pp. 69–95.

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

[7] G. S. Bales and A. Zangwill, Phys. Rev. B **41**, 5500 (1990).

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

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

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

[11] D. Kandel and J. D. Weeks, Phys. Rev. B **49**, 5554 (1994).

[12] W. F. Chung and M. S. Altman, Phys. Rev. B **66**, 075338 (2002).

[13] A. Pimpinelli and A. Videcoq, Surf. Sci. Lett. **445**, L23 (2000).

[14] A. Pimpinelli, A. Videcoq, and M. Vladimirova, Appl. Surf. Sci. **175**, 55 (2001).

[15] M. Vladimirova, A. Pimpinelli, and A. Videcoq, J. Cryst. Growth **220**, 631 (2000).

[16] S. Stoyanov, Jpn. J. Appl. Phys., Part 1 **30**, 1 (1991).

[17] P. Politi and J. Krug, Surf. Sci. **446**, 89 (2000).

[18] N. Néel, T. Maroutian, L. Douillard, and H.-J. Ernst, Phys. Rev. Lett. **91**, 226103 (2003).

[19] J. Mysliveček, C. Schelling, G. S. F. Schäffler, P. Šmilauer, J. Krug, and B. Voigtländer, Surf. Sci. **520**, 193 (2002).

[20] P. Cermelli and M. E. Jabbour, Proc. R. Soc. London, Ser. A **461**, 3483 (2005).

[21] J. Tersoff, M. D. Johnson, and B. G. Orr, Phys. Rev. Lett. **78**, 282 (1997).

[22] D. W. Kisker, G. B. Stephenson, J. Tersoff, P. H. Fuoss, and S. Brennan, J. Cryst. Growth **163**, 54 (1996).

[23] B. D. Coleman and W. Noll, Arch. Ration. Mech. Anal. **13**, 167 (1963).

[24] M. E. Gurtin and P. W. Voorhees, Acta Mater. **44**, 235 (1996).

[25] E. Fried and M. E. Gurtin, J. Stat. Phys. **95**, 1361 (1999).

[26] E. Fried and M. E. Gurtin, J. Mech. Phys. Solids **51**, 487 (2003).

[27] E. Fried and M. E. Gurtin, Adv. Appl. Mech. **40**, 1 (2004).