

A STEP-FLOW MODEL FOR THE HETERO-EPITAXIAL GROWTH OF STRAINED, SUBSTITUTIONAL, BINARY ALLOY FILMS WITH PHASE SEGREGATION: I.THEORY*

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Abstract. We develop a step-flow model for the hetero-epitaxy of a generic, strained, substitutional, binary alloy. The underlying theory is based on the fundamental principles of modern continuum thermodynamics. In order to resolve the inherent disparity in the spatial scales—continuous in the lateral directions vs. atomistically discrete along the epitaxial axis—, we represent the film as a layered structure, with the layer height equal to the lattice parameter along the growth direction, thus extending the classical BCF framework [BURTON, CABRERA, & FRANK. The growth of crystals and the equilibrium of their surfaces. *Phil. Trans. Roy. Soc. London A*, **243** (1951) 299–358] to growth situations in which the bulk behaviour impacts on the surface evolution. Our discrete-continuum model takes the form of a free-boundary problem for the evolution of monoatomic steps on a vicinal surface, in which interfacial effects on the terraces and along the step edges couple to their bulk counterparts (i.e., within both film and, indirectly, substrate). In particular, the proposed constitutive theory is such that the film layers are endowed with (generalized) Ginzburg–Landau free energies that account for phase segregation and, concomitantly, competition between gradient-driven coarsening and elastic refining of the separated domains. Importantly, the bulk and terrace effects are intertwined with the step dynamics via novel boundary conditions at the step edges derived from separate balance laws for configurational and micro-forces. Specifically, the former forces are associated with the evolution of defects (in the present setting, the steps) whereas the latter forces accompany micro- and nano-scopic changes in an order parameter (for a binary alloy subject to diffusion-mediated phase separation, the atomic density of one of its components or, equivalently, the relative atomic density), and the postulated balances should be viewed as generalizations to a dynamic, dissipative setting—such as epitaxial growth, a far-from-equilibrium process—of more standard variational calculations.

Key words. Epitaxy, multiscale, multispecies, discrete-continuum, step dynamics, surface-bulk coupling, substitutional alloy, phase segregation, coarsening, refining, Ginzburg–Landau, atomic diffusion, linear elasticity, configurational forces, order parameter, microforces.

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1. Introduction. The growth of thin solid films by molecular beam epitaxy (MBE) is known to yield high-quality surfaces, i.e., ones characterized by well defined crystallographic orientations. Correspondingly, the morphological evolution of such surfaces during deposition has long been a major focus of attention in surface science, cf., e.g., TSAO [1], VAN DER EERDEN [2], SAITO [3], PIMPINELLI & VILLAIN [4], JEONG & WILLIAMS [5]. Indeed, the quasi-planar shape of growing vicinal surfaces can be significantly altered by instabilities of various types. In the context of applica-

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tions for which a planar morphology is desirable, e.g., for hetero-junctions in semiconductor devices, such instabilities are considered detrimental. (The role of theory there is to investigate the existence of growth regimes for which these instabilities can be entirely suppressed.) In contrast, if the goal is the processing of nanostructures—e.g., quantum dots and wires—via the deposition of self-organizing films, then the same instabilities come to be viewed as beneficial by crystal growers as they provide an alternative to the more standard materials-patterning technologies. In either case, a better mathematical understanding of the onset and evolution of such instabilities is crucial. Specifically, these instabilities are geometric (i.e., curvature-driven), kinetic (e.g., of the Ehrlich–Schwoebel, cf. SCHWOEBEL & SHIPSEY [6] and EHRLICH & HUDDA [7], or of the Bales–Zangwill type, cf. BALES & ZANGWILL [8]), and thermodynamic (i.e., energetic) in nature, and the interplay between the underlying physical and/or chemical mechanisms during growth is still not completely understood, particularly in the context of multispecies epitaxy. The present work aims at deriving a thermodynamically consistent, continuum-discrete model for the hetero-epitaxial growth of a generic thin solid film made of a substitutional binary alloy, viewed as a layered nanostructure and whose surface evolves via step flow.¹ Of chief interest are phase segregation and the ensuing competition between coarsening—which results from the incorporation of a gradient term into the bulk free-energy density that penalizes abrupt spatial variations in chemical composition—and elastically driven refining of the separated domains within the film and substrate. We begin with a brief discussion of the literature, both theoretical and experimental.²

1.1. Homo-epitaxy. During homo-epitaxy, in which a thin film of a pure substance is deposited upon a substrate of the same material, the morphological evolution of the film surface is governed solely by processes which occur locally, i.e., at the surface and in its immediate vicinity (this is the so-called interface-controlled growth regime). As originally proposed by BURTON, CABRERA, & FRANK [10] (referred to below as the BCF model), the growth process can be effectively described by the nucleation, advancement, and annihilation of monatomic steps. Mediated by the diffusive transport of adatoms on the terraces and their attachment-detachment kinetics along the step edges, these mechanisms provide the basis for a $(2+1)$ -dimensional description of surface evolution, i.e., two-dimensional in the lateral directions and one-dimensional along the growth axis. Most importantly, such a framework embeds a coarse-grained atomistic description of the steps, accounting in particular for edge kinetic effects, within a continuum formalism whose range of validity encompasses large time and length scales³. (For recent work on finer atomistic descriptions of step

¹At sufficiently elevated temperatures, but below the roughening temperature, high adatom mobilities insure that diffusion towards and attachment to the steps of the vicinal surface are the predominant growth mechanisms. Accordingly, the nucleation and growth of monatomic-high islands—resulting from collisions between adatoms, dimers, trimers, etc., during random walk—on the terraces can be ignored. Hence the assumption that growth occurs exclusively via step flow. Moreover, it is expected that at high temperatures bulk atomic diffusion is activated and, in the presence of a double-well bulk potential, phase separation ensues (cf. the more detailed discussion below).

²The list of articles reviewed herein is by no means exhaustive. Indeed, there exists a large body of literature on epitaxial crystal growth that spans several decades of research and encompasses a wide variety of methodologies, from atomistics to continuum. (A good starting point would be the books by TSAO [1], SAITO [3], and PIMPINELLI & VILLAIN [4], and/or the review articles by VAN DER EERDEN [2], JEONG & WILLIAMS [5], and KRUG [9].) Nevertheless, the novel features of the proposed theory have no direct antecedents as is discussed below.

³The BCF formalism has become paradigmatic of the study of surface evolution during epitaxy. For recent reviews of step dynamics in the setting of homo-epitaxy and the resulting morphological

kinetics within the BCF formalism, cf., e.g., CAFLISCH ET AL. [12] and BALYKOV & VOIGT [13, 14].) Our goal here is to extend the discrete-continuum BCF formalism to growth situations where the bulk behaviour impacts on the step-mediated surface evolution. We propose to do so by modeling the film as a *layered* nanostructure with the interfaces between adjacent layers as fictitious extensions of the flat terraces (cf. Fig. 2.1).

1.2. Hetero-epitaxy. In contrast, during hetero-epitaxy, film and substrate are made of different materials, e.g., Si on Ge, or possibly of the same material but with different compositions, e.g., a film consisting of a generic binary alloy $A_\alpha B_{1-\alpha}$ deposited upon a substrate made of the same alloy but with different stoichiometry $A_\delta B_{1-\delta}$ ($\alpha \neq \delta$). In either case, a misfit stress is generated as a result of the discrepancy in lattice parameters between film and substrate, and the ensuing competition between surface tension and bulk strain-energy is known to influence the film growth, with the former inhibiting the growth of instabilities and the latter favoring the formation, via adatom diffusion, of surface undulations that relieve the stress (as established for single-component systems by ASARO & TILLER [15], GRINFELD [16], SROLOVITZ [17], and SPENCER, VOORHEES, & DAVIS [18]).⁴ During alloy growth, this competition is rendered more intricate by the presence of multiple chemical species and the ensuing phase segregation (cf., e.g., LÉONARD & DESAI [22] and the references therein). From the point of view of applications, controlling the onset and evolution of stress-driven instabilities during the epitaxy of self-assembling crystalline films paves the way to the systematic (rather than ad hoc) processing of nanoscale structures, e.g., quantum dots and wires, ordered two-dimensional patterns, lateral multilayers, etc. This in turn is contingent on a better understanding of the interplay between bulk elasticity, chemical composition, and surface mechanisms. Below is a concise survey of previous studies pertaining to the impact on the surface morphology of the interaction between chemical composition and strain-energy.

1.2.1. Film composition and strain-energy. During the growth of strained alloy films, compositional inhomogeneities within the bulk and on the surface are known to affect the morphological evolution of the latter.⁵ In SPENCER, VOORHEES, & TERSOFF [23, 24], this influence is traced back to two distinct features of the underlying atomic structure of the growing film, namely the different atomic radii of the alloy components and the differences in adatom mobilities, and it is established that, for adatoms of distinct radii and mobilities, a growth regime exists for which morphological and compositional instabilities can be suppressed. But these studies do not consider phase separation within the bulk or on the surface of the growing film,⁶ a growth feature for which there is ample experimental evidence. The coupling between atomic ordering (alloying), phase segregation, and stress-driven morphological

instabilities, cf. KRUG [9] and PIERRE-LOUIS [11].

⁴Bulk strain-energy is a central ingredient of continuum theories of hetero-epitaxial growth. Indeed, as mentioned above, the difference in the film and substrate lattice parameters generates a mismatch strain and, correspondingly, a misfit stress. An alternative mechanism by which the lattice mismatch is relieved resides in the formation of dislocations that are generated on the film-substrate interface, cf., e.g., KUKTA & FREUND [19], FREUND [20], and FREUND & SURESH [21]. Herein we confine our attention to coherent substrate-film interface and hence assume that the film is dislocation-free.

⁵Indeed, compositional non-uniformities lead to (i) solute stresses which in turn trigger the formation of island-like structures on the surface, and (ii) variations in the elastic coefficients and surface energy, hence contributing to the competition between interfacial and strain energies.

⁶In particular, bulk atomic diffusion is ignored, see also GUYER & VOORHEES [25, 26].

instabilities is, on the other hand, the subject of LÉONARD & DESAI [27, 28, 29], a series of articles in which the focus is on the growth of binary alloys such that the two species are simultaneously deposited (a setting we shall also consider herein).⁷ These theoretical studies are augmented by several recent experiments involving phase segregation in compositionally inhomogeneous crystalline (sub)monolayers that indicate a strong dependence of concentration on strain energy, cf., e.g., POHL ET AL. [31], TOBER ET AL. [32], and THAYER ET AL. [33]. The stability of the observed two-dimensional, phase-segregated domains was first investigated by MARCHENKO [34] and NG & VANDERBILT [35], and more recently by LU & SUO [36, 37] and KIM & LU [38] with the aim of characterizing pattern formation during the deposition of epilayers. Specifically, the observed patterns result from the interplay between two competing mechanisms: coarsening, due to the presence of a phase-boundary free energy, and elastically driven refining. Finally, additional evidence of nanoscale pattern formation was obtained via quantitative first-principles calculations, cf. OZOLINS, ASTA, & HOYT [39], and kinetic Monte Carlo simulations, cf. VOLKMANN ET AL. [40].

Despite the great impact that they have had on our understanding of the coupled effects of elasticity and chemical composition on the morphological stability of alloy films and epilayers, these studies, whether of a continuum nature or based on an atomistic methodology, suffer from certain limitations. Specifically, the ones that consider growth dynamics do so either at the mesoscale—i.e., by assuming that the film surface is a smooth, time-dependent, two-dimensional manifold—with the consequence that the role of the finer details of the surface nanostructure such as steps is not accounted for, or for perfectly flat surfaces—i.e., neglecting surface fluctuations altogether, a reasonable assumption only in the context of epilayer growth—, whereas the remaining studies are confined to equilibrium situations. But, because phase segregation and the ensuing pattern formation occur during MBE growth, and given that the latter proceeds, at high temperatures, via the motion of steps, it is essential for the understanding of the onset and evolution of stress-induced instabilities in alloy films at the *nanoscale* to examine the interplay between chemical composition and misfit strain in the dynamic setting of *step-flow* growth.

1.2.2. Stress-induced instabilities and the flow of steps. Various experiments indicate that the early stages of the stress-induced self-assembly of faceted three-dimensional islands are related to the merging of steps on the film surface, cf., e.g., SUTTER & LAGALLY [41] and TROMP, ROSS, & REUTER [42]. Specifically, the spacing between steps gradually decreases until the sidewalls of the developing pyramids attain certain crystallographic orientations. In SHENNOY & FREUND [43], these observations serve as a basis for the formulation of a continuum theory for the emergence of islands whose key ingredients are elastic step-step interactions and a dependence of the step free energy on the mismatch strain. Changes in composition, however, have not been considered. Moreover, that step flow plays a direct role in the alloying (chemical ordering) of thin films has only recently been experimentally put in evidence, cf. HANNON ET AL. [44] in which it is observed that the intermixing of components during growth is enhanced on stepped surfaces and hindered on terraces where step flow does not occur. Importantly, as alluded to above, a theoretical understanding of the role of steps during alloy epitaxy is still lacking. The model proposed

⁷Note that the resulting concentration modulations are also achieved by alternately depositing different materials or, when one material is deposited upon another, via vertical exchange mechanisms by which the substrate constituents remain present on the growing surface. Cf., e.g., BIERWALD ET AL. [30].

herein is an attempt in that direction.

1.3. A step-flow model for alloy growth. Main results. In this article, we present a discrete-continuum theory for the hetero-epitaxial, step-flow growth of substitutional, binary alloys which couples surface (i.e., terrace and step) effects with bulk (i.e., film and substrate) atomic transport and elasticity. Our goal is to provide a thermodynamically compatible framework within which to investigate alloy formation (i.e., intermixing and phase segregation), surface-morphology evolution, and their interplay in the context of multicomponent film growth. Of chief interest are the equations that govern the evolution of steps. Indeed, it is these equations that couple the diffusion-mediated phase separation within the film layers to the step dynamics.

1.3.1. Step-flow growth of multispecies films. We briefly recall several attempts to extend the classical BCF model to the case of multiple species, with and without strain relaxation. Step-flow growth situations in which two distinct, chemically reacting species are deposited upon a rigid substrate⁸ have been investigated in JABBOUR & BHATTACHARYA [45], PIMPINELLI & VIDECCOCQ [46], PIMPINELLI, VIDECCOCQ, & VLADIMIROVA [47], and PIMPINELLI ET AL. [48]. In particular, all three models share the rather restrictive assumption that the growing crystal consists of just one type of (real or effective) particles formed via a chemical reaction, either along the steps or on the terraces, between adatoms of the two deposited materials. Hence, there is no atomic diffusion within the film and, subsequently, the issue of coupling surface and bulk mechanisms is simply irrelevant in that context. A more general theory of multispecies epitaxy that incorporates step anisotropy, allows for departures from local equilibrium, and accounts for general chemical kinetics in a way consistent with the second law, but is equally oblivious of the bulk phase is proposed by CERMELLI & JABBOUR [49].⁹ In contrast, the model developed in JABBOUR [50] accounts explicitly for the coupling between bulk and surface as well as phase separation, but it does not allow for either coarsening or refining of the formed domains (i.e., its formulation precludes elasticity, and its constitutive provisions do not permit a gradient-dependent bulk free energy). Moreover, it differs from the present model in that it accounts only indirectly for the discrete structure of the film along the growth direction, whereas our layered structure, by extending the vicinal surface's terraces into virtual interfaces between monolayers within the film, allows for an explicit discrete-continuum description of the growth process. Finally, we note that strain relaxation in a discrete-continuum framework has only recently been considered by SCHINDLER ET AL. [51], where an atomistic model is used to describe elasticity; in contrast, our approach is based on standard continuum elasticity formulated on an atomistic grid.

1.3.2. Main results: bulk and surface evolution equations. The main contribution of the proposed model resides in the coupled PDE's that govern the dynamics of steps on the film vicinal surface. As noted above, these equations couple the evolution of steps to (a) the equations that govern the adsorption-desorption and diffusive transport of adatoms on the terraces and to (b) the equations that describe bulk atomic diffusion and elasticity. The former take the form of reaction-diffusion PDE's on the terraces whereas the latter, when supplemented by constitutive prescriptions for the bulk free-energy densities of the Ginzburg–Landau type, reduce to

⁸I.e., one within which the stress is indeterminate.

⁹Specifically, it is assumed that the bulk atomic densities of the alloy components are constant.

discrete-continuum Cahn–Hilliard equations, intertwined with the mechanical equilibrium equations (also in a hybrid discrete-continuum form), within the film layers and substrate. Specifically, along each step, the evolution equations consist of (i) *species jump conditions* that account for both diffusive and convective contributions to the adatom fluxes from the adjacent terraces into the steps,¹⁰ (ii) a *continuity-of-traction condition* that complements the bulk mechanical-equilibrium equations, (iii) a *chemical interface-condition* that ensures the continuity of the *relative* chemical potential across each step, (iv) a *configurational force balance* which, when constitutively augmented by Eshelby-type relations, yields a “kinetic relation” that prescribes the step velocity as a function of the thermodynamic driving force acting on it, (v) a *microforce balance* which provides, over and above the species conservation equations, a supplemental boundary condition for the Cahn–Hilliard equation within the upper layer terminating at the given step, and finally (vi) a *total atomic-density balance*.¹¹

Consider the step-flow growth of a *binary* substitutional alloy. Let ρ_i^k denote the density of adatoms of the k -th species ($k = 1, 2$) on the i -th terrace ($i = 1, \dots, N$), μ_i^k the corresponding chemical potential, $\rho_{i,b}^{12}$ and $\mu_{i,b}^{12}$ the *relative* atomic density and chemical potential within the i -th layer of the film respectively ($\rho_{i,b}^{12} := \rho_{i,b}^1 - \rho_{i,b}^2$ and $\mu_{i,b}^{12} := \mu_{i,b}^1 - \mu_{i,b}^2$), \mathbf{u}_i the (two-dimensional) displacement within the i -th layer, and \mathbf{E}_i the corresponding linearized, discrete-continuum strain tensor (as defined in (3.11)). Finally, denote by $\rho_{-1,b}^{12}$, $\mu_{-1,b}^{12}$, \mathbf{u}_{-1} , and \mathbf{E}_{-1} the relative atomic density, relative chemical potential, (three-dimensional) displacement field, and the linearized strain tensor within the substrate.

- Upon the i -th terrace ($1 \leq i \leq N$), the k -th species balance ($k = 1, 2$) takes the form of a reaction-diffusion equation:

$$\partial_t \rho_i^k - \operatorname{div} \left\{ \mathbf{L}_i^k \nabla \mu_i^k \right\} = \mathbf{F}^k - \gamma_i^k \mu_i^k, \quad (1.1)$$

where $\mathbf{L}_i^k = \mathbf{L}^k(\rho_{i-1,b}^{12})$, \mathbf{F}^k , and $\gamma^k = \gamma^k(\rho_{i-1,b}^{12})$ are the terrace atomic mobility, deposition flux, and desorption coefficient of k -adatoms respectively.¹²

¹⁰For simplicity, we choose to neglect step adatom densities, i.e., the steps are endowed with a thermodynamic structure but are not allowed to sustain mass. Furthermore, the terrace adatom diffusion is assumed to be isotropic and interspecies coupling is ignored. For a general theory that allows for anisotropic terrace adatom diffusion and accounts for edge adatom densities and anisotropy as well as step and terrace chemical reactions, cf. CERMELLI & JABBOUR [49].

¹¹Regarding the physical significance of (iv) and (v), a few remarks are in order. Configurational forces are associated with the evolution of defects—here the steps—and we take the point of view that they satisfy a separate balance law (cf., e.g., GURTIN [52, 53] and the references therein). The latter, when localized to an evolving step and constitutively augmented, yields a generalization to multispecies systems of the classical Gibbs–Thomson condition, one that does not require local equilibrium along the step edges and is hence appropriate for dynamic, dissipative settings such as the present one. On the other hand, microforces accompany the changes in an order parameter—in the case of a phase-segregating binary alloy, the bulk density of one of its two components or, equivalently, the relative atomic density—and, following GURTIN [54], we again postulate that they obey a separate balance. Within each layer of the film, combining the microforce and species balances yields a Cahn–Hilliard-type equation (coupled, as mentioned above, with the standard force balance). Because it is fourth-order, the Cahn–hilliard equation requires a supplemental boundary condition at the step that terminates the bulk layer in question. This additional condition is obtained by localizing the microforce balance at the step and augmenting it constitutively.

¹²In a departure from more standard theoretical treatments of MBE, we assume that the atomic mobility and desorption coefficient depend on the chemical composition of the layer immediately below the i -th terrace. Moreover, we shall neglect interspecies coupling, so that the evaporation and diffusive fluxes of k -adatoms are functions exclusively of the chemical potential associated with the k -th species and its gradient respectively.

Furthermore, the k -th chemical potential is specified by

$$\mu_i^k = \partial_{\rho_i^k} \Psi_i,$$

with $\Psi_i = \Psi(\rho_i^1, \rho_i^2)$ the terrace free-energy density (per unit area).¹³

- Within the i -th film layer ($i = 0, \dots, N-1$), the species balances combine to yield a discrete-continuum diffusion equation for the *relative* density:

$$\partial_t \rho_{i,b}^{12} - \operatorname{div} \{ \mathbf{L}_{i,b}^{12} \nabla \mu_{i,b}^{12} \} = \alpha_{i-1} \frac{\mathbf{L}_{i-1,b}^{12} \mu_{i-1,b}^{12} - \mathbf{L}_{i,b}^{12} \mu_{i,b}^{12}}{a^2} - \alpha_i \frac{\mathbf{L}_{i,b}^{12} \mu_{i,b}^{12} - \mathbf{L}_{i+1,b}^{12} \mu_{i+1,b}^{12}}{a^2}, \quad (1.2)$$

where $\mathbf{L}_{i,b}^{12} = \mathbf{L}_b^{12}(\rho_{i,b}^{12}; i)$, the relative bulk atomic mobility within the i -th layer, depends on the (local) chemical composition and is a decaying function of the distance to the surface, and the relative chemical potential is specified by

$$\mu_{i,b}^{12} = -\epsilon \Delta \rho_{i,b}^{12} + \partial_{\rho_{i,b}^{12}} \Psi_{i,b}^*(\rho_{i,b}^{12}) + \partial_{\rho_{i,b}^{12}} \mathbf{W}(\rho_{i,b}^{12}, \mathbf{E}_i(\mathbf{u}_{i-1}, \mathbf{u}_i)) - \epsilon \left\{ \alpha_{i-1} \frac{\rho_{i-1,b}^{12} - \rho_{i,b}^{12}}{a^2} - \alpha_i \frac{\rho_{i,b}^{12} - \rho_{i+1,b}^{12}}{a^2} \right\}, \quad (1.3)$$

with $\Psi_{i,b}^*$ a double-well potential that defines the two segregated phases and \mathbf{W} the strain-energy density associated with the i -th layer, a the lattice parameter along the growth direction, ϵ a small parameter, and $\alpha_i = 1$ for both i and $i+1$ within the bulk, $\alpha_i = 0$ otherwise.¹⁴ Finally, letting \mathbf{e}_3 denote the unit vector along the growth direction pointing upward and $\mathbb{P}_3 := \mathbf{1} - \mathbf{e}_3 \otimes \mathbf{e}_3$ the projection of \mathbb{R}^3 onto \mathbb{R}^2 , eqts. (1.2) and (1.3) are coupled to the mechanical-equilibrium condition:¹⁵

$$\operatorname{div} \{ \mathbb{P}_3 \mathbf{T}_i \} + \frac{1}{2} \sum_{n=1}^3 \left\{ \alpha_{i-1} \frac{\mathbf{T}_{i-1}^{n3} - \mathbf{T}_i^{n3}}{a} + \alpha_i \frac{\mathbf{T}_i^{n3} - \mathbf{T}_{i+1}^{n3}}{a} \right\} \mathbf{e}_3 = \mathbf{0}, \quad (1.4)$$

with $\mathbf{T}_i^{nm} := \mathbf{e}_n \cdot \mathbf{T}_i \mathbf{e}_m$ ($n, m \in \{1, 2, 3\}$) and \mathbf{T}_i , the (three-dimensional) stress tensor within the i -th layer, constitutively prescribed by

$$\mathbf{T}_i = \partial_{\mathbf{E}_i} \mathbf{W}(\rho_{i,b}^{12}, \mathbf{E}_i(\mathbf{u}_{i-1}, \mathbf{u}_i)), \quad (1.5)$$

¹³We shall assume that the i -th terrace consists of a ternary regular solution, its three components being the two species of adatoms and the empty adsorption sites. Then, letting w_k denote the energy per interatomic bond associated with an adatom of the k -th species ($k = 1, 2$), the terrace free-energy density (per unit area) is given by

$$\Psi(\rho_i^1, \rho_i^2) = \hat{\Psi}(\theta_i^1, \theta_i^2) = 4(w_1 \theta_i^1 + w_2 \theta_i^2)(1 - \theta_i^1 - \theta_i^2) + k_B T \{ \theta_i^1 \ln \theta_i^1 + \theta_i^2 \ln \theta_i^2 + (1 - \theta_i^1 - \theta_i^2) \ln(1 - \theta_i^1 - \theta_i^2) \},$$

with $\theta_i^k := \frac{\rho_i^k}{\rho_{\text{sites}}}$ the coverage density of the i -th terrace by adatoms of the k -th species and ρ_{sites} the density (per unit area) of lattice sites, k_B the Boltzmann constant, and T the (fixed) temperature.

¹⁴Given the lattice constraint for a binary substitutional alloy, $\rho_{i,b}^1 + \rho_{i,b}^2 = \rho_{\text{sites}}$, $\Psi_{i,b}^* = \Psi_b^*(\rho_{i,b}^1, \rho_{i,b}^2)$ reduces to $\Psi_{i,b}^* = \tilde{\Psi}_b^*(\rho_{i,b}^{12})$. Similarly, the stored-energy density can be made to depend only on the relative density within the i -th layer, $\mathbf{W} = \mathbf{W}(\rho_{i,b}^1, \rho_{i,b}^2, \mathbf{E}_i) = \tilde{\mathbf{W}}(\rho_{i,b}^{12}, \mathbf{E}_i)$.

¹⁵Since thin film growth and related instabilities occur on a time scale slow in comparison with material sound speeds, we neglect inertia within both film and substrate.

and \mathbf{E}_i , the discrete-continuum, infinitesimal strain tensor, defined by

$$\mathbf{E}_i := \frac{1}{2} \{ \nabla \mathbf{u}_i + (\nabla \mathbf{u}_i)^T \} + \frac{1}{2} \alpha_{i-1} \left\{ \frac{\mathbf{u}_{i-1} - \mathbf{u}_i}{a} \otimes \mathbf{e}_3 + \mathbf{e}_3 \otimes \frac{\mathbf{u}_{i-1} - \mathbf{u}_i}{a} \right\}. \quad (1.6)$$

- Within the substrate (itself a substitutional binary alloy made of the same two chemical constituents), the governing equations consist of a bulk diffusion equation for the relative density:

$$\partial_t \rho_{-1,b}^{12} - \operatorname{div}_3 \{ \mathbf{L}_{-1,b}^{12} \nabla_3 \mu_{-1,b}^{12} \} = 0, \quad (1.7)$$

with $\mathbf{L}_{-1,b}^{12} = \mathbf{L}_{-1,b}^{12}(\rho_{-1,b}^{12})$ the substrate relative atomic mobility, augmented by the constitutive prescription of the substrate relative chemical potential:

$$\mu_{-1,b}^{12} = -\epsilon \Delta_3 \rho_{-1,b}^{12} + \partial_{\rho_{-1,b}^{12}} \Psi_{-1,b}^*(\rho_{-1,b}^{12}) + \partial_{\rho_{-1,b}^{12}} \mathbf{W}(\rho_{-1,b}^{12}, \mathbf{E}_{-1}(\mathbf{u}_{-1})), \quad (1.8)$$

and supplemented by balance of standard forces:

$$\operatorname{div}_3 \mathbf{T}_{-1} = \mathbf{0}. \quad (1.9)$$

Here the subscript 3 denotes the three-dimensional gradient (∇_3), divergence (div_3), and Laplacian (Δ_3), as opposed to their two-dimensional counterparts within the film layers, and \mathbf{T}_{-1} , the stress tensor within the substrate, constitutively prescribed by

$$\mathbf{T}_{-1} = \partial_{\mathbf{E}_{-1}} \mathbf{W}(\rho_{-1,b}^{12}, \mathbf{E}_{-1}(\mathbf{u}_{-1})). \quad (1.10)$$

- Along the i -th step ($1 \leq i \leq N$), the k -th species jump conditions reduce to:

$$\left. \begin{aligned} \mathbf{K}_{i,+}^k \{ (\mu_{i-1}^k)^+ - \mu_{i,s}^k \} &= (\rho_{i-1}^k)^+ V_i + \mathbf{L}_{i-1}^k (\nabla \mu_{i-1}^k)^+ \cdot \mathbf{n}_i, \\ \mathbf{K}_{i,-}^k \{ (\mu_i^k)^- - \mu_{i,s}^k \} &= -(\rho_i^k)^- V_i - \mathbf{L}_i^k (\nabla \mu_i^k)^- \cdot \mathbf{n}_i. \end{aligned} \right\} \quad (1.11)$$

Here \mathbf{n}_i is the unit normal to the i -th step pointing into the $(i-1)$ -th terrace and V_i its normal velocity;

$$\mathbf{K}_{i,+}^k = \mathbf{K}_+^k(\Theta_i, (\rho_{i-1,b}^{12})^-, \rho_{i-2,b}^{12}) \quad \text{and} \quad \mathbf{K}_{i,-}^k = \mathbf{K}_-^k(\Theta_i, (\rho_{i-1,b}^{12})^-, \rho_{i-2,b}^{12})$$

are the non-negative kinetic coefficients for the attachment-detachment of k -adatoms from the lower and upper terraces onto the i -th step edge respectively, with Θ_i the angle between \mathbf{n}_i and an in-plane reference axis; $\mu_{i,s}^k$ is the chemical potential associated with k -adatoms along the i -th step; and the $+$ ($-$) superscript denotes limiting values as the i -th step is approached from the $(i-1)$ -th (i -th) terrace. Eqts. (1.11)_{1,2} are supplemented by the so-called chemical interface-condition that ensures the continuity of the relative chemical potential across the i -th step:¹⁶

$$\mu_{i,s}^1 - \mu_{i,s}^2 = (\mu_{i-1,b}^{12})^-, \quad (1.12)$$

and coupled to the continuity-of-traction condition:¹⁷

$$\{ \mathbb{P}_3 \mathbf{T}_{i-1} \}^- \cdot \mathbf{n}_i = \mathbf{0}. \quad (1.13)$$

¹⁶Cf. FRIED & GURTIN [55], eqt. (23.1).

¹⁷In eqts. (1.12) and (1.13), the $-$ superscript denotes limiting values as the i -th step is approached from within the $(i-1)$ -th layer, i.e., the layer that terminates at the i -th step (cf. Fig. 2.1).

where \mathbf{T}_{i-1} is given by (1.5)–(1.6). Furthermore, letting $\gamma_i = \gamma(\Theta_i)$ denote the i -th step free energy (per unit length), the interfacial conditions (1.11)–(1.13) are complemented by a kinetic relation¹⁸ that results from constitutively augmenting the normal configurational force balance along the step:¹⁹

$$\llbracket \omega \rrbracket_i - (\Psi_{i-1,b})^- + \sum_{k=1}^2 \mu_{i,s}^k \rho_{i-1,b}^k + \tilde{\gamma}_i \kappa_i = \beta_{is} V_i, \quad (1.14)$$

where $\llbracket \omega \rrbracket_i = \omega_i^+ - \omega_{i-1}^-$ is the jump in the terrace grand canonical potential, $\omega_i = \Psi_i - \sum_{k=1}^2 \mu_i^k \rho_i^k$, across the i -th terrace, and $\Psi_{i-1,b}$ is the Helmholtz free-energy density (per unit area) of the i -th layer; $\tilde{\gamma}_i = \gamma + \frac{\partial^2 \gamma}{\partial \Theta_i^2}$ is the step stiffness; and $\beta_{i,s} = \beta(\Theta_i, (\rho_{i-1,b}^{12})^-, \rho_{i-2,b}^{12})$ is the i -th step kinetic modulus.²⁰ In addition, the microforce balance, when localized to the i -th step, takes the form:

$$\epsilon(\nabla \rho_{i-1,b}^{12})^- \cdot \mathbf{n}_i = -\alpha_i (\partial_t \rho_{i-1,b}^{12})^-, \quad (1.15)$$

with $\alpha_i = \alpha(\Theta_i, (\rho_{i-1,b}^{12})^-, \rho_{i-2,b}^{12})$ a non-negative material parameter that characterizes the step response to interfacial microforces. Finally, closure is brought upon the step evolution equations by the *total* atomic balance which, in the absence of edge diffusion, writes as:

$$\begin{aligned} \rho^{\text{sites}} V_i = & \sum_{k=1}^2 \mathbf{K}_{i,+}^k \{(\mu_{i-1}^k)^+ - \mu_{i,s}^k\} \\ & + \sum_{k=1}^2 \mathbf{K}_{i,-}^k \{(\mu_i^k)^- - \mu_{i,s}^k\} + \sum_{k=1}^2 \partial_\varsigma \left\{ \mathbf{L}_{i,s}^k \partial_\varsigma \mu_{i,s}^k \right\}, \end{aligned} \quad (1.16)$$

with ς the arclength parameter along $\Gamma_i(t)$ and $\mathbf{L}_{i,s}^k = \mathbf{L}_s^k(\Theta_i, (\rho_{i-1,b}^{12})^-, \rho_{i-2,b}^{12})$ the non-negative edge atomic mobility.

- Finally, letting the film-substrate interface coincide with the $\{x_3 = 0\}$ -plane and assuming that the relative chemical potential is continuous across the film-substrate boundary,

$$\mu_{0,b}^{12} = \mu_{-1,b}^{12} \Big|_{x_3=0},$$

the balance for the relative atomic density takes the form

$$\frac{\mathbf{L}_{0,b}^{12} \mu_{0,b}^{12} - \mathbf{L}_{1,b}^{12} \mu_{1,b}^{12}}{a} = (\mathbf{L}_{-1,b}^{12} \nabla_3 \mu_{-1,b}^{12}) \Big|_{x_3=0} \cdot \mathbf{e}_3, \quad (1.17)$$

¹⁸Cf., e.g., ABEYARATNE & KNOWLES [56].

¹⁹For a general discussion of configurational forces as primitive fields of continuum physics, cf. GURTIN [57, 52, 53] and the references therein. For a discussion of the role of configurational forces during epitaxy, cf. FRIED & GURTIN [58, 55] and JABBOUR & BHATTACHARYA [59]. On the role of configurational forces in step-flow growth, cf. CERMELLI & JABBOUR [49] and JABBOUR [50].

²⁰Note that the kinetic modulus for the i -th step is dependent on both step orientation and chemical composition, the former via Θ_i and the latter through the limiting value of $\rho_{i-1,b}^{12}$ as the step edge is approached from within the $(i-1)$ -th layer, $Q_{i-1}(t)$, as well as $\rho_{i-2,b}^{12}$, the relative atomic density within $Q_{i-2}(t)$. By contrast, when the edge adatom densities are negligible, the second law restricts the step free-energy density to depend solely on its orientation, cf. Section 4 and, in particular, the dissipation inequality (4.12) and the discussion that follows.

augmented by the continuity-of-traction condition:

$$\mathbf{T}_0 \cdot \mathbf{e}_3 = \mathbf{T}_{-1}|_{x_3=0} \cdot \mathbf{e}_3, \quad (1.18)$$

with \mathbf{T}_0 and \mathbf{T}_{-1} prescribed by (1.5)–(1.6) and (1.10) respectively, and complemented by the microforce balance:

$$\epsilon \left\{ \frac{\rho_{0,b}^{12} - \rho_{1,b}^{12}}{a} - \nabla_3 \rho_{-1,b}^{12}|_{x_3=0} \cdot \mathbf{e}_3 \right\} = \alpha_+ \partial_t \rho_{0,b}^{12} + \alpha_- \partial_t \rho_{-1,b}^{12}|_{x_3=0}, \quad (1.19)$$

with $\alpha_+ = \alpha_+(\rho_{-1,b}^{12}|_{x_3=0}, \rho_{0,b}^{12})$ and $\alpha_- = \alpha_-(\rho_{-1,b}^{12}|_{x_3=0}, \rho_{0,b}^{12})$ non-negative material parameters that characterize the response of the film-substrate interface to microforces.

Outline. The remainder of the paper proceeds as follows. Section 2 introduces basic notation and motivates the representation of the growing film as a layered structure at the nanoscale. In Section 3, we list and discuss the coupled PDE's that form the skeleton of the proposed free-boundary problem for the step positions, focusing only on the key ingredients.²¹ Section 4 is mainly concerned with the thermodynamic consistency of the model. Section 5 contains a brief discussion of the theory. Finally, Appendix A discusses consistency with BCF models for single-species films.

2. Notation. The film as a layered nanostructure. To model epitaxy one needs to consider the atomic deposition fluxes onto a vicinal surface, the diffusion of the adsorbed atoms (adatoms) over the terraces, and eventually their desorption back into the adjacent vacuum. Moreover, the terrace adatoms may aggregate to form nuclei, which would then grow into monatomic island, or they might attach directly to pre-existing steps along whose edges they can diffuse. Furthermore, in the presence of multiple species, chemical reactions can occur on the terraces and along the steps, as well as atomic diffusion and phase segregation within the bulk phase. Finally, during hetero-epitaxy, strain effects need to be incorporated. Multispecies epitaxial growth can thus be described by the advancement, nucleation, and/or annihilation of steps, and its mathematical formulation reduces to a free-boundary problem for the evolving step positions. Importantly, the boundary conditions along the steps need to account not only for surface—i.e., terraces and steps—mechanisms but should also couple these with the behaviour of the film's bulk.

We denote by $\Omega \subset \mathbb{R}^2$ the projected domain of the film surface onto a two-dimensional Cartesian coordinate system, and assume that Ω is independent of time t . Furthermore, let $\Omega_i = \Omega_i(t) \subset \mathbb{R}^2$ ($i = 0, \dots, N$) be the projected domain of the terrace of height i at time t , and define $\Gamma_i = \Gamma_i(t) = \bar{\Omega}_i(t) \cap \bar{\Omega}_{i-1}(t)$ ($i = 1, \dots, N$) to be the projected (smooth) curve corresponding to the step separating the adjacent terraces of heights i and $i-1$.²² The surface thus viewed delimits the film which we represent as an atomistically layered structure, and we label $Q_i = Q_i(t) \subset \mathbb{R}^2$ ($i = 0, \dots, N-1$) the projected domain of the bulk layer terminating at the $(i+1)$ -th step edge, such that $Q_i(t) = \cup_{j>i} \Omega_j(t)$. Finally, let $Q_{-1} \subset \mathbb{R}^3$ denote the substrate, see Fig. 2.1.

²¹For the details of the derivation that yields the pointwise evolution equations from the integral statements of the balance laws of continuum thermodynamics, we refer the reader to JABBOUR & VOIGT [60].

²²Importantly, the steps are assumed to be monatomic and the terraces flat. Correspondingly, the thickness of the film layers equals the interatomic distance along the growth direction. Hence the terrace heights are indexed using the integer i .

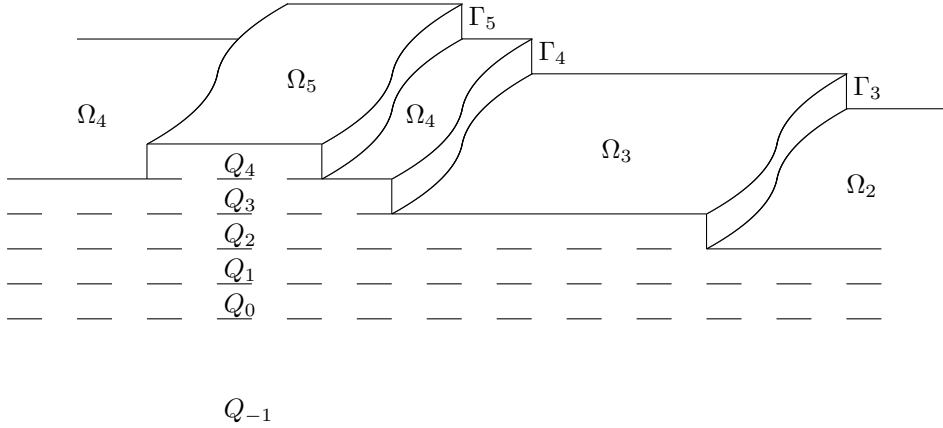


FIG. 2.1. Schematic representation of a vicinal surface together with the underlying layered film and the substrate.

Our view is that the layered film structure is needed to model step-flow-mediated heteroepitaxial growth because the evolution of the i -th step, $\Gamma_i(t)$, is governed not only by the behaviour of the adjacent upper and lower terraces, $\Omega_i(t)$ and $\Omega_{i-1}(t)$ respectively, but also by the mechanisms at play within the film—and, indirectly, the substrate—, i.e., within the ascending layer $Q_{i-1}(t)$. Thus the key idea is to describe the bulk as a continuum within the substrate, i.e., away from the surface, but as a discrete-continuum atomistically layered structure within the growing film, i.e., in the vicinity of the surface. Specifically, the discrete layers in the film are introduced for two reasons: (i) they allow to resolve the disparate spatial scales in the horizontal and vertical directions, and (ii) they provide the natural geometrical framework within which to model the exchange processes between adatoms on the terraces and atoms in the bulk through the attachment-detachment and absorption kinetics along the steps.

Basic notation. The subscripts s and b denote quantities defined along the step edges and within the bulk, the latter term encapsulating both film and substrate. The superscript k refers to the k -th species (for a binary system, $k = 1, 2$), whereas the subscript i refers to a field or material parameter defined along the i -th step, on the i -th terrace, or within the i -th layer, with $i = -1$ for the substrate. E.g., $\rho_i^k(x_1, x_2, t)$ and $\mu_i^k(x_1, x_2, t)$ stand for the density of k -adatoms on the i -th terrace $\Omega_i(t)$ and the associated chemical potential respectively (as functions of the in-plane Cartesian coordinates x_1 and x_2 and time t), while $\rho_{i,b}^k(x_1, x_2, t)$ and $\mu_{i,b}^k(x_1, x_2, t)$ represent their counterparts within the film's i -th layer $Q_i(t)$; $\rho_{-1,b}^k(x_1, x_2, x_3, t)$ and $\mu_{-1,b}^k(x_1, x_2, x_3, t)$ the k -th atomic density and chemical potential within the substrate, with x_3 the coordinate along the growth direction; and $\mu_{i,s}^k(\zeta, t)$ the k -th chemical potential along the i -th step edge, where the variable ζ denotes the arclength parameter; etc.

3. Step-flow growth of a binary, substitutional-alloy film. For simplicity, we restrict attention to the binary case, i.e., $k = 1, 2$. To highlight the key ingredients of the theory, we merely list the governing PDE's, leaving the details of the derivations to JABBOUR & VOIGT [60]. In essence, our model requires the specification of (i)

the dynamics of terrace-atom transport, (ii) the dynamics of bulk atomic diffusion within the film layers and substrate, coupled to the mechanical-equilibrium conditions, (iii) the evolution equations that govern the far-from-equilibrium motion of steps, and (iv) the jump conditions on the film-substrate interface. We first turn to the terrace dynamics.

3.1. Terrace adatom transport. We assume that there are no advancies on the terraces. Hence we ignore the exchange of atoms between the terraces and the underlying bulk layers, and confine the flow of adatoms into the film to the step edges. Letting ρ_i^k , μ_i^k , and $\rho_{i-1,b}^{12}$ denote the density of k -adatoms ($k = 1, 2$) on the i -th terrace ($i = 1, \dots, N$), its associated chemical potential, and the relative atomic density within the $(i-1)$ -th layer (i.e., the one underlying the i -th terrace), the k -th species balance upon the i -th terrace reduces to a reaction-diffusion PDE:

$$\underbrace{\partial_t \rho_i^k - \operatorname{div} \left\{ \mathbf{L}_i^k \nabla \mu_i^k \right\}}_{\text{diffusion}} = \underbrace{\mathbf{F}^k - \gamma_i^k \mu_i^k}_{\text{adsorption-desorption}} \quad \text{on } \Omega_i(t). \quad (3.1)$$

Here \mathbf{F}^k is the deposition flux of atoms of the k -th species; $\mathbf{L}_i^k = \mathbf{L}^k(\rho_{i-1,b}^{12})$ and $\gamma^k = \gamma^k(\rho_{i-1,b}^{12})$ are the atomic mobility and desorption coefficient of k -adatoms on the i -th terrace, both assumed to be non-negative functions of the chemical composition of $Q_{i-1}(t)$, the layer immediately below the i -th terrace; and μ_i^k , the k -th chemical potential on the i -th terrace, is given by:

$$\mu_i^k = \partial_{\rho_i^k} \Psi_i, \quad (3.2)$$

with $\Psi_i = \Psi(\rho_i^1, \rho_i^2)$ the terrace free-energy density (per unit area). A few remarks are in order. First, we ignore the nucleation of new islands.²³ In addition, we assume that adatom diffusion is isotropic and neglect interspecies coupling, so that the evaporation and diffusive fluxes of k -adatoms on the i -th terrace, \mathbf{R}_i^k and \mathbf{h}_i^k respectively, are functions exclusively of the k -th chemical potential and its gradient, i.e., $\mathbf{R}_i^k = -\gamma_i^k \mu_i^k$ and $\mathbf{h}_i^k = -\mathbf{L}_i^k \nabla \mu_i^k$.²⁴ Furthermore, as mentioned above, we neglect the exchange of atoms between the terrace and the underlying bulk layer, an approximation that is consistent with the assumption that there are no advancies on the terraces. Hence adatom incorporation into the bulk occurs solely along the steps. Finally, we shall assume that the i -th terrace consists of a ternary regular solution, its three constituents being the adatoms of the two deposited chemical species and the empty adsorption sites. Hence, letting w_1 and w_2 be the bond strengths associated with adatoms of type 1 and 2, and denoting by ρ^{sites} the density of lattice sites (per unit area), the

²³See Footnote 2, p. 2. In order to incorporate island nucleation, the framework developed by POLITI & CASTELLANO [61, 62] has to be generalized to the case of multiple species.

²⁴A constitutive theory for the terraces that allows for anisotropic adatom diffusion and permits interspecies coupling would be based on the stipulations

$$\mathbf{R}_i^k = - \sum_{j=1}^2 \gamma_i^{kj} \mu_i^j \quad \text{and} \quad \mathbf{h}_i^k = - \sum_{j=1}^2 \mathbf{L}_i^{kj} \nabla \mu_i^j,$$

where $\gamma_i^{kj} \geq 0$ and the 2×2 mobility matrices \mathbf{L}_i^{kj} satisfy $\sum_{j=1}^2 \nabla \mu_i^k \cdot \mathbf{L}_i^{kj} \nabla \mu_i^j \geq 0$.

terrace free-energy density (per unit adsorption site) is given by:

$$\Psi_i = \Psi(\rho_i^1, \rho_i^2) = \hat{\Psi}(\theta_i^1, \theta_i^2) = \underbrace{4(w_1\theta_i^1 + w_2\theta_i^2)(1 - \theta_i^1 - \theta_i^2)}_{\text{internal energy}} + \underbrace{k_B T \left\{ \theta_i^1 \ln \theta_i^1 + \theta_i^2 \ln \theta_i^2 + (1 - \theta_i^1 - \theta_i^2) \ln(1 - \theta_i^1 - \theta_i^2) \right\}}_{-T \times (\text{entropy of mixing})}, \quad (3.3)$$

where $\theta_i^k := \frac{\rho_i^k}{\rho_{\text{sites}}^k}$ is the k -adatom coverage of the i -th terrace, k_B the Boltzmann constant, and T the temperature (assumed constant, as we consider only isothermal growth).²⁵ By (3.2), it follows that

$$\frac{\mu_i^k}{\rho_{\text{sites}}^k} = 4w_k \left(1 - 2 \sum_{j=1}^2 \theta_i^j \right) + k_B T \ln \left\{ \frac{\theta_i^k}{1 - \sum_{j=1}^2 \theta_i^j} \right\}. \quad (3.4)$$

Hence, although seemingly uncoupled, the reaction-diffusion equations (3.1) are intertwined via the constitutive relations that specify the terrace species chemical potentials (3.4).

3.2. Bulk atomic diffusion and elasticity. Contrary to their terrace counterparts, the bulk atomic densities are not independent. Indeed, within each layer $Q_i(t)$ ($i = 0, \dots, N$), letting ρ^{sites} denote the density of lattice sites (per unit area), $\rho_{i,b}^1$ and $\rho_{i,b}^2$ are subject to the lattice constraint:

$$\rho_{i,b}^1 + \rho_{i,b}^2 = \rho^{\text{sites}}. \quad (3.5)$$

Introducing $\rho_{i,b}^{12} := \rho_{i,b}^1 - \rho_{i,b}^2$ and $\mu_{i,b}^{12} := \mu_{i,b}^1 - \mu_{i,b}^2$, the relative atomic density and chemical potential in the i -th layer, (3.5) can be used to reduce the system of diffusion equations for $\rho_{i,b}^1$ and $\rho_{i,b}^2$ to a single discrete-continuum diffusion equation:

$$\partial_t \rho_{i,b}^{12} - \text{div} \{ L_{i,b}^{12} \nabla \mu_{i,b}^{12} \} = \alpha_{i-1} \frac{L_{i-1,b}^{12} \mu_{i-1,b}^{12} - L_{i,b}^{12} \mu_{i,b}^{12}}{a^2} - \alpha_i \frac{L_{i,b}^{12} \mu_{i,b}^{12} - L_{i+1,b}^{12} \mu_{i+1,b}^{12}}{a^2} \quad \text{within } Q_i(t), \quad (3.6)$$

where $L_{i,b}^{12} = L_b^{12}(\rho_{i,b}^{12}; i)$, the relative bulk atomic mobility within the i -th layer, depends on the (local) chemical composition and is a decaying function of the distance to the surface (cf. TU & TERSOFF [63]), a is the layer thickness, and $\alpha_i = 1$ if both the i - and $(i+1)$ -layers are within the bulk and $\alpha_i = 0$ otherwise. Importantly, the right-hand side of (3.6) models diffusion along the growth direction (and, hence, encapsulates atomic exchange processes between adjacent layers) in a discrete fashion. It can be viewed as a finite difference approximation of the second derivative along the vertical direction on a grid with an atomistic resolution.²⁶

²⁵The statistical-mechanical argument that yields the constitutive relation (3.3) extends to the binary case the more standard calculation of the free energy per surface site when the deposited adatoms belong to the same species, cf. TSAO [1, pp. 203-204].

²⁶Both α_i and α_{i-1} equal one within the bulk. Thus the right-hand side of (3.6) is the exact approximation of the second derivative. But, in the absence of a bulk layer at height $(i+1)$, α_i vanishes. This is tantamount to a no-flux boundary condition at the surface and is consistent with our assumption that the exchange of atoms between bulk and surface is confined to the steps.

The diffusion equation (3.6) is complemented by the balance of linear momentum which, when inertia is neglected, reduces to the mechanical-equilibrium condition:

$$\operatorname{div} \mathbf{T}_i + \frac{1}{2} \sum_{n=1}^3 \left\{ \alpha_{i-1} \frac{T_{i-1}^{n3} - T_i^{n3}}{a} + \alpha_i \frac{T_i^{n3} - T_{i+1}^{n3}}{a} \right\} \mathbf{e}_3 = \mathbf{0} \quad \text{within } Q_i(t), \quad (3.7)$$

with \mathbf{T}_i the Cauchy stress tensor associated with the i -th layer, α_i and α_{i-1} defined as above, and \mathbf{e}_3 the unit vector along the growth direction. The right-hand side of (3.7) can again be viewed as a finite difference approximation of the divergence operator in the vertical direction on a grid with an atomistic resolution.

The discrete-continuum diffusion equation (3.6) and the mechanical-equilibrium conditions (3.7) are coupled through the constitutive prescription of the bulk free-energy density (per unit area) associated with the i -th layer. Indeed, the latter takes the form of a generalized Ginzburg–Landau functional:²⁷

$$\Psi_{i,b} = \frac{1}{2} \epsilon \nabla \rho_{i,b}^{12} \cdot \nabla \rho_{i,b}^{12} + \Psi_{i,b}^*(\rho_{i,b}^{12}) + W(\rho_{i,b}^{12}, \mathbf{E}_i(\mathbf{u}_{i-1}, \mathbf{u}_i)) + \frac{\epsilon}{2} \left\{ \alpha_{i-1} \frac{\rho_{i-1,b} - \rho_{i,b}}{a} - \alpha_i \frac{\rho_{i,b} - \rho_{i+1,b}}{a} \right\}^2, \quad (3.8)$$

where ϵ is a given, small parameter; $\Psi_{i,b}^*$ is a *double-well potential* that defines the two segregated phases within $Q_i(t)$ viewed as a binary regular solution whose constituents are the two incorporated species:²⁸

$$\Psi_{i,b}^*(\rho_{i,b}^{12}) = \hat{\Psi}_{i,b}^*(c_{i,b}^{12}) = (1 - c_{i,b}^{12}) \Psi_1 + c_{i,b}^{12} \Psi_2 + \underbrace{\rho_{\text{sites}} k_B T \{ c_{i,b}^{12} \ln c_{i,b}^{12} + (1 - c_{i,b}^{12}) \ln(1 - c_{i,b}^{12}) \}}_{-T \times (\text{entropy of mixing})} + \underbrace{\rho_{\text{sites}} \Omega c_{i,b}^{12} (1 - c_{i,b}^{12})}_{\text{energy of mixing}}, \quad (3.9)$$

with Ψ_1 (Ψ_2) the excess energy when the i -th layer is made entirely of atoms of the first (second) species, $c_{i,b}^{12} := \frac{1}{2} \left\{ 1 - \frac{\rho_{i,b}^{12}}{\rho_{\text{sites}}^{12}} \right\}$ the concentration of atoms of the 2-nd species within the i -th layer, and Ω a material parameter that measures bond strength relative to the thermal energy;²⁹ the strain-energy density is constitutively specified by

$$W(\rho_{i,b}^{12}, \mathbf{E}_i(\mathbf{u}_{i-1}, \mathbf{u}_i)) = \frac{1}{2} \{ \mathbf{E}_i - \mathbf{E}^*(\rho_{i,b}^{12}) \} \cdot \mathbb{C}(\rho_{i,b}^{12}) \{ \mathbf{E}_i - \mathbf{E}^*(\rho_{i,b}^{12}) \}, \quad (3.10)$$

with $\mathbb{C}(\rho_{i,b}^{12})$ the composition-dependent (fourth-order) elasticity tensor; and $\mathbf{E}_i = \mathbf{E}_i(\mathbf{u}_{i-1}, \mathbf{u}_i)$ is the discrete-continuum, linearized strain tensor:

$$\mathbf{E}_i := \frac{1}{2} \{ \nabla \mathbf{u}_i + (\nabla \mathbf{u}_i)^T \} + \frac{1}{2} \alpha_{i-1} \left\{ \frac{\mathbf{u}_{i-1} - \mathbf{u}_i}{a} \otimes \mathbf{e}_3 + \mathbf{e}_3 \otimes \frac{\mathbf{u}_{i-1} - \mathbf{u}_i}{a} \right\}, \quad (3.11)$$

where $\mathbf{u}_i = \sum_{j=1}^2 u_i^j(x_1, x_2) \mathbf{e}_j$ is the two-dimensional displacement within the i -th layer, $\mathbf{E}^*(\rho_{i,b}^{12})$ is the stress-free strain when the i -th layer chemical composition is

²⁷The quadratic-gradient term on the right-hand side of (3.8) is regularizing in that it penalizes abrupt spatial variations in the (relative) atomic density within the layer. Moreover, the last term on the RHS of (3.8) can be viewed as a discretized approximation of the gradient term along the epitaxial direction.

²⁸Cf., e.g., TSAO [1] and LU & SUO [36].

²⁹For Ω sufficiently large, $\Psi_{i,b}^*$ has two wells and hence drives phase separation.

given by $\rho_{i,b}^{12}$ and, as before, the last two terms on the right-hand side of (3.11) model the strain components along the growth direction in a discrete fashion. Importantly, the two-dimensionality of the i -th displacement field, $\mathbf{u}_i \cdot \mathbf{e}_3 = 0$, is needed to ensure that the interfaces that separate adjacent layers remain flat. However, it does not imply that either strain or stress is plane. Indeed, in view of (3.11), the only zero strain component is $E_i^{33} := \mathbf{e}_3 \cdot \mathbf{E}_i \mathbf{e}_3$ and, by (3.13) below, the stress tensor is fully three-dimensional. Importantly, the stress tensor \mathbf{T}_i is constitutively prescribed by

$$\mathbf{T}_i = \partial_{\mathbf{E}_i} W(\rho_{i,b}^{12}, \mathbf{E}_i(\mathbf{u}_{i-1}, \mathbf{u}_i)) \quad (3.12)$$

which, in view of (3.10), reduces to

$$\mathbf{T}_i = \mathbb{C}(\rho_{i,b}^{12}) \{ \mathbf{E}_i - \mathbf{E}^*(\rho_{i,b}^{12}) \}. \quad (3.13)$$

Moreover, the relative chemical potential is given by

$$\mu_{i,b}^{12} = \partial_{\rho_{i,b}^{12}} \Psi_i - \operatorname{div} \left\{ \partial_{\nabla \rho_{i,b}^{12}} \Psi_i \right\}, \quad (3.14)$$

which, when combined with (3.8), yields:³⁰

$$\begin{aligned} \mu_{i,b}^{12} = & -\epsilon \Delta \rho_{i,b}^{12} + \partial_{\rho_{i,b}^{12}} \Psi_{i,b}^* + \partial_{\rho_{i,b}^{12}} W(\rho_{i,b}^{12}, \mathbf{E}_i(\mathbf{u}_{i-1}, \mathbf{u}_i)) \\ & - \epsilon \left\{ \alpha_{i-1} \frac{\rho_{i-1,b}^{12} - \rho_{i,b}^{12}}{a^2} - \alpha_i \frac{\rho_{i,b}^{12} - \rho_{i+1,b}^{12}}{a^2} \right\}. \end{aligned} \quad (3.15)$$

3.3. The substrate: atomic diffusion, mechanical equilibrium, and the jump conditions at the film-substrate interface. We assume that the substrate is made of the same binary, substitutional alloy as the growing film. Hence the species atomic densities, $\rho_{-1,b}^1$ and $\rho_{-1,b}^2$, are subject to a lattice constraint similar to (3.5):

$$\rho_{-1,b}^1 + \rho_{-1,b}^2 = \rho_{-1}^{\text{sites}}, \quad (3.16)$$

where ρ_{-1}^{sites} is the number of lattice sites per unit volume. We also assume that the three-dimensional region it occupies, $Q_{-1} \subset \mathbb{R}^3$, coincides with the lower half-space so that the film-substrate interface coincides with the (x_1, x_2) -plane.³¹ Let $\rho_{-1,b}^{12}$ and $\mu_{-1,b}^{12}$ denote the relative atomic density and chemical potential within the substrate. The species equations combine into a diffusion equation for the relative density:

$$\partial_t \rho_{-1,b}^{12} - \operatorname{div}_3 \{ L_{-1,b}^{12} \nabla_3 \mu_{-1,b}^{12} \} = 0 \quad \text{in } Q_{-1}, \quad (3.17)$$

with $L_{-1,b}^{12} = L_{-1,b}^{12}(\rho_{-1,b}^{12})$ the composition-dependent, relative, atomic mobility within the substrate. Here, the subscript 3 refers to the three-dimensional divergence and gradient (as opposed to their two-dimensional, subscript-free counterparts within the film layers and on the terraces). As before, atomic diffusion is assumed isotropic

³⁰As shown in GURTIN [54] and JABBOUR & VOIGT [60], this relation can be derived from a balance of microforces. Together with (3.6), it yields a Cahn-Hilliard type equation for $\rho_{i,b}^{12}$.

³¹Implicit is the assumption that the film-substrate interface remains planar throughout deposition. This is consistent with (i) our assumption that the displacement field within the zeroth layer, $Q_0(t)$, is two-dimensional, i.e., $\mathbf{u}_0 \cdot \mathbf{e}_3 = 0$, and (ii) the assumption that the film-substrate interface is coherent, i.e., $\mathbf{u}_0(x_1, x_2) = \lim_{\epsilon \rightarrow 0^+} \mathbf{u}_{-1}(x_1, x_2, -\epsilon)$.

and interspecies coupling is ignored. Eq. (3.17) is supplemented by the mechanical equilibrium condition:

$$\operatorname{div}_3 \mathbf{T}_{-1} = \mathbf{0} \quad \text{inside } Q_{-1}, \quad (3.18)$$

where \mathbf{T}_{-1} denotes the the Cauchy stress tensor within Q_{-1} . The coupling between (3.17) and (3.18) occurs, as within the film layers, via the constitutive prescription of the substrate free-energy density (per unit volume):

$$\Psi_{-1,b} = \frac{1}{2} \epsilon \nabla_3 \rho_{-1,b}^{12} \cdot \nabla_3 \rho_{-1,b}^{12} + \Psi_{-1,b}^*(\rho_{-1,b}^{12}) + W(\rho_{-1,b}^{12}, \mathbf{E}_{-1}). \quad (3.19)$$

Here, as in (3.8), the first term on the right-hand side of (3.19) penalizes rapid spatial oscillations of the substrate chemical composition. Furthermore, assuming that the substrate behaves like a binary, regular solution, $\Psi_{-1,b}^*$, the free-energy density at zero stress, is a temperature-dependent, double-well potential whose wells define the separated phases within the substrate:

$$\begin{aligned} \Psi_{-1,b}^*(\rho_{-1,b}^{12}) &= \hat{\Psi}_{-1,b}^*(c_{-1,b}^{12}) = (1 - c_{-1,b}^{12}) \Psi_{-1,b}^1 + c_{-1,b}^{12} \Psi_{-1,b}^2 \\ &+ \underbrace{\rho_{-1}^{\text{sites}} k_B T \{c_{-1,b}^{12} \ln c_{-1,b}^{12} + (1 - c_{-1,b}^{12}) \ln(1 - c_{-1,b}^{12})\}}_{-T \times (\text{entropy of mixing})} + \underbrace{\rho_{-1}^{\text{sites}} \Omega c_{-1,b}^{12} (1 - c_{-1,b}^{12})}_{\text{energy of mixing}}, \end{aligned} \quad (3.20)$$

with $\Psi_{-1,b}^1$ ($\Psi_{-1,b}^2$) the excess energy (per unit volume) when the substrate consists entirely of atoms of the first (second) species, $c_{-1,b}^{12} := \frac{1}{2} \left\{ 1 - \frac{\rho_{-1,b}^{12}}{\rho_{-1}^{\text{sites}}} \right\}$ the concentration of substrate atoms of the 2-nd species, and Ω defined as above.³² Finally, consistent with the linear-elasticity assumption, the stored-energy density is specified as a quadratic, composition-dependent, function of the infinitesimal strain:

$$W(\rho_{-1,b}^{12}, \mathbf{E}_{-1}) = \{ \mathbf{E}_{-1} - \mathbf{E}^*(\rho_{-1,b}^{12}) \} \cdot \mathbb{C}(\rho_{-1,b}^{12}) \{ \mathbf{E}_{-1} - \mathbf{E}^*(\rho_{-1,b}^{12}) \}, \quad (3.21)$$

with $\mathbb{C}(\rho_{-1,b}^{12})$ defined as above, \mathbf{E}_{-1} the linearized strain tensor given by

$$\mathbf{E}_{-1} := \frac{1}{2} \{ \nabla_3 \mathbf{u}_{-1} + (\nabla_3 \mathbf{u}_{-1})^\top \}, \quad (3.22)$$

and $\mathbf{E}^*(\rho_{-1,b}^{12})$ the solute strain when the substrate composition is given by $\rho_{-1,b}^{12}$. In view of (3.19), (3.20), and (3.21), it follows that the stress tensor, given by

$$\mathbf{T}_{-1} = \partial_{\mathbf{E}_{-1}} \Psi_{-1,b} = \partial_{\mathbf{E}_{-1}} W, \quad (3.23)$$

takes the form

$$\mathbf{T}_{-1} = \mathbb{C}(\rho_{-1,b}^{12}) \{ \mathbf{E}_{-1} - \mathbf{E}^*(\rho_{-1,b}^{12}) \}, \quad (3.24)$$

whereas the relative chemical potential, specified by

$$\mu_{-1,b}^{12} = \partial_{\rho_{-1,b}^{12}} \Psi_{-1,b} - \operatorname{div}_3 \left\{ \partial_{\nabla_3 \rho_{-1,b}^{12}} \Psi_{-1,b} \right\}, \quad (3.25)$$

³²As for (3.8), for Ω sufficiently large, $\Psi_{-1,b}^*$ has two wells and hence drives phase separation.

reduces to

$$\mu_{-1,b}^{12} = -\epsilon \Delta_3 \rho_{-1,b}^{12} + \partial_{\rho_{-1,b}^{12}} \Psi_{i,b}^* + \partial_{\rho_{-1,b}^{12}}, \quad (3.26)$$

with Δ_3 the three-dimensional Laplacian. Importantly, the injection of the constitutive relation (3.26) into (3.17) yields a three-dimensional, Cahn–Hilliard-type PDE for the substrate relative atomic density (viewed as an order parameter). Moreover, appealing to (3.24) and (3.26), it can be seen that the coupling between atomic diffusion, governed by (3.17), and elasticity, described by (3.18), resides in the dependence of the stress on the substrate chemical composition and, conversely, of the relative chemical potential on strain.

Boundary conditions on the film-substrate interface. At the interface between the zeroth film layer, Q_0 , and the substrate, Q_{-1} , the mechanical-equilibrium PDE's (3.18) are complemented by the continuity-of-traction condition

$$(\mathbf{T}_0 - \mathbf{T}_{-1})|_{x_3=0} \mathbf{e}_3 = \mathbf{0}, \quad (3.27)$$

with \mathbf{e}_3 the unit vector along the growth direction (pointing upward), \mathbf{T}_0 the stress tensor within the zeroth layer, cf. eqts. (3.12) and (3.13), and \mathbf{T}_{-1} is the substrate stress tensor, cf. (3.23) and (3.24).³³

Furthermore, as mentioned above, the substrate diffusion eqt., (3.17), when constitutively augmented by (3.26), yields a fourth-order PDE for the relative atomic density $\rho_{-1,b}^{12}$ of the Cahn–Hilliard type. As such, (3.17) requires the specification of two boundary conditions at the film-substrate interface. These boundary conditions result from the localization of the atomic-density and the microforce balances. Assuming that the relative chemical potential is continuous across the film-substrate boundary,

$$\mu_{0,b}^{12} = \mu_{-1,b}^{12}|_{x_3=0}, \quad (3.28)$$

the former takes the form

$$\frac{L_{0,b}^{12} \mu_{0,b}^{12} - L_{1,b}^{12} \mu_{1,b}^{12}}{a} = (L_{-1,b}^{12} \nabla_3 \mu_{-1,b}^{12})|_{x_3=0} \cdot \mathbf{e}_3, \quad (3.29)$$

whereas the latter reduces to

$$\epsilon \left\{ \frac{\rho_{0,b}^{12} - \rho_{1,b}^{12}}{a} - \nabla_3 \rho_{-1,b}^{12}|_{x_3=0} \cdot \mathbf{e}_3 \right\} = \alpha_+ \partial_t \rho_{0,b}^{12} + \alpha_- \partial_t \rho_{-1,b}^{12}|_{x_3=0}, \quad (3.30)$$

with $\alpha_+ = \alpha_+(\rho_{-1,b}^{12}|_{x_3=0}, \rho_{0,b}^{12})$ and $\alpha_- = \alpha_-(\rho_{-1,b}^{12}|_{x_3=0}, \rho_{0,b}^{12})$ non-negative material parameters that characterize the response of the film-substrate interface to microforces.³⁴

3.4. Step evolution equations. Central to our theory are the step evolution equations. Indeed, these equations couple the step dynamics to the transport of terrace adatoms and to the atomic diffusion and mechanics of film layers (and, indirectly, to the latter's counterparts within the substrate).

³³Eq. (3.27) results from the localization, in the absence of inertia, of the linear-momentum conservation principle.

³⁴As before, the left-hand side of (3.29) and the first term on the left-hand side of (3.30) can be interpreted as finite-difference approximations of the film's relative diffusive flux and atomic-density gradient respectively along the growth (vertical) direction on an atomistic-resolution grid.

Terrace-step coupling: the species jump conditions. Letting $J_{i,+}^k$ and $J_{i,-}^k$ denote the (scalar) flows of adatoms of the k -th species ($k = 1, 2$) into the i -th step edge ($i = 1, \dots, N$) from the $(i-1)$ -th (lower) and i -th (upper) terraces respectively, the k -th species atomic-density balances on the adjacent domains $\Omega_{i-1}(t)$ and $\Omega_i(t)$, when localized at $\Gamma_i(t)$, yield the jump conditions:

$$\left. \begin{aligned} J_{i,+}^k &= (\rho_{i-1}^k)^+ V_i + L_{i-1}^k (\nabla \mu_{i-1}^k)^+ \cdot \mathbf{n}_i, \\ J_{i,-}^k &= -(\rho_i^k)^- V_i - L_i^k (\nabla \mu_i^k)^- \cdot \mathbf{n}_i, \end{aligned} \right\} \quad (3.31)$$

with \mathbf{n}_i the unit normal to the i -th step pointing into the $(i-1)$ -th (lower) terrace and V_i its normal velocity, and the superscripts $+$ and $-$ label limiting values as the i -th step is approached from the lower and upper adjacent terraces respectively. The simplest constitutive expressions for $J_{i,+}^k$ and $J_{i,-}^k$ consistent with the second law are given by (cf. Section 4 below):

$$\left. \begin{aligned} J_{i,+}^k &= K_{i,+}^k \{ (\mu_{i-1}^k)^+ - \mu_{i,s}^k \}, \\ J_{i,-}^k &= K_{i,-}^k \{ (\mu_i^k)^- - \mu_{i,s}^k \}, \end{aligned} \right\} \quad (3.32)$$

where

$$K_{i,+}^k = K_+^k (\Theta_i, (\rho_{i-1,b}^{12})^-, \rho_{i-2,b}^{12}) \quad \text{and} \quad K_{i,-}^k = K_-^k (\Theta_i, (\rho_{i-1,b}^{12})^-, \rho_{i-2,b}^{12})$$

are the non-negative kinetic coefficients for the attachment-detachment of k -adatoms from the lower and upper terraces onto the i -th step edge respectively, Θ_i is the angle between \mathbf{n}_i and an in-plane reference crystalline axis, and $\mu_{i,s}^k$ denotes the chemical potential associated with k -adatoms along the i -th step. Here, as for the transport of adatoms on the terraces, interspecies coupling is neglected.³⁵

Bulk-step coupling: continuity of the relative chemical potential, jump condition for the relative atomic density, standard and microforce balances.

When, as is assumed herein, the edge adatom densities are ignored, the step species chemical potentials are indeterminate.³⁶ For simplicity, we shall assume that the i -th step, $\Gamma_i(t)$, is in local chemical equilibrium with the adjacent $(i-1)$ -th bulk layer, $Q_{i-1}(t)$. Given that the film is made of a substitutional alloy, only the relative chemical potential has meaning within the film (cf. LARCHÉ & CAHN [64, 65], CAHN

³⁵Even in the context of *single-species* growth and assuming that adatom attachment-detachment to the step edges is *isotropic*, an asymmetry in the kinetic coefficients, i.e., $K_{i,+} \neq K_{i,-}$, is known to dramatically impact on the morphological stability of stepped surfaces. E.g., in the presence of an Ehrlich-Schwoebel effect, i.e., when attachment is energetically more favorable for adatoms approaching a given step from its lower adjacent terrace, a one-dimensional train of equidistant steps will remain as such during deposition, although step bunching will occur during sublimation, cf., e.g., PIMPINELLI & VILLAIN [4] and KRUG [9]. Conversely, in the presence of an *inverse* Ehrlich-Schwoebel barrier, i.e., when $K_{i,+} < K_{i,-}$, such a train of steps will become unstable to linear perturbations. Moreover, this kinetic asymmetry plays a critical role in step meandering, cf., e.g., BALES & ZANGWILL [8]. Finally, when the steps act as adatom sinks, i.e., in the limiting case when $K_{i,\pm}^k \rightarrow \infty$, the terrace chemical potentials become continuous and, concomitantly, the adatom flows, $J_{i,+}^k$ and $J_{i,-}^k$, are rendered indeterminate. Hence eqts. (3.31) reduce to what sometimes are referred to as thermodynamic boundary conditions:

$$\mu_i^k = \mu_{i,s}^k = \mu_{i-1}^k.$$

³⁶This is in contrast with the terrace chemical potentials which are prescribed by the constitutive relations (3.2).

& LARCHÉ [66], and the discussion of FRIED & GURTIN [55]). Hence the local chemical-equilibrium condition reduces to the requirement that the relative chemical potential be continuous along the i -th step ($1 \leq i \leq N$):

$$\mu_{i,s}^1 - \mu_{i,s}^2 = \mu_{i-1,b}^{12}. \quad (3.33)$$

Importantly, this continuity condition implies that the inflow of edge adatoms into the bulk is now identically zero. It follows that the relative atomic-density balance within $Q_{i-1}(t)$, when localized along the i -th step, takes the form:

$$(\rho_{i-1,b}^{12})^- V_i = - (\mathbf{L}_{i-1,b}^{12} \nabla \mu_{i-1,b}^{12})^- \cdot \mathbf{n}_i, \quad (3.34)$$

i.e., the diffusive flux of atoms from the $(i-1)$ -th layer is converted entirely into the convective motion of the i -th step edge.

In addition, neglecting standard stress along the step, the mechanical-equilibrium condition within the film's $(i-1)$ -th layer, when localized to the i -step yields

$$\mathbf{T}_{i-1} \mathbf{n}_i = \mathbf{0}, \quad (3.35)$$

which states that the i -th step is traction-free. Here, the stress is constitutively specified by (3.13).

Microforce balance. In the presence of diffusion within the crystalline bulk, the relative atomic density $\rho_{i,b}^{12}$ can be viewed as an order parameter whose evolution governs phase segregation within the i -th film layer. We take the point of view that associated with changes in $\rho_{i,b}^{12}$ are microforces which, following GURTIN [54], are assumed to satisfy a separate balance law. Specifically, we postulate the existence, within the i -th layer $Q-i(t)$, of a microforce vector-stress $\boldsymbol{\varepsilon}_{i,b}$ and a microforce scalar-force $\pi_{i,b}$, and, along the i -th step edge $\Gamma_i(t)$, of an interfacial scalar-force $\xi_{i,s}$, such that the microforce balance, when localized within the film layers and along the step edges, yields

$$\left. \begin{aligned} \operatorname{div} \boldsymbol{\varepsilon}_{i-1,b} + \pi_{i-1,b} &= 0 && \text{in } Q_{i-1}(t), \\ -(\boldsymbol{\varepsilon}_{i-1,b})^- \cdot \mathbf{n}_i + \xi_{i,s} &= 0 && \text{along } \Gamma_i(t), \end{aligned} \right\} \quad (3.36)$$

with $(\boldsymbol{\varepsilon}_{i-1,b})^-$ the limiting value of $\boldsymbol{\varepsilon}_{i-1,b}$ as the i -th step is approached from within the $(i-1)$ -th layer. Consistency with the second law imposes the following relations (cf. JABBOUR & VOIGT [60]):

$$\left. \begin{aligned} \pi_{i,b} &= \mu_{i,b}^{12} - \partial_{\rho_{i,b}^{12}} \Psi_{i,b}, \\ \boldsymbol{\varepsilon}_{i,b} &= \partial_{\nabla \rho_{i,b}^{12}} \Psi_{i,b}, \\ \xi_{i,s} &= -\alpha_{i,s} (\rho_{i-1,b}^{12})^-, \end{aligned} \right\} \quad (3.37)$$

where, accounting for the step anisotropy, $\alpha_{i,s} = \alpha_{i,s}((\rho_{i-1,b}^{12})^-, \Theta_i)$ is a non-negative, composition-dependent, scalar coefficient. Substitution of (3.37)_{1,2} into (3.36)₁ yields the identity between $\mu_{i,b}^{12}$ and the variational derivative of $\Psi_{i,b}$ with respect to the relative atomic density, cf. (3.14). Moreover, when the free-energy density of the i -th layer is specified by (3.8), the relative chemical potential within the i -th layer reduces to (3.15) which, if substituted back into the atomic diffusion equation for the i -th layer, (3.6), yields a discrete-continuum PDE within $Q_i(t)$ of the Cahn–Hilliard type. Being of fourth-order, such an equation requires the specification of

two boundary conditions along $\Gamma_{i+1}(t)$, i.e., the step that terminates the i -th layer. One such boundary condition results from the localization of (3.6) along the step, cf. eqt. (3.34). The remaining condition is furnished by (3.36)₂. Indeed, when constitutively augmented by (3.37)_{2,3}, the interfacial microforce balance reduces to

$$\epsilon (\nabla \rho_{i-1,b}^{12})^- \cdot \mathbf{n}_i = -\alpha_{i,s} (\partial_t \rho_{i-1,b}^{12})^- \quad (3.38)$$

where it was further assumed that the free-energy density for the i -th layer ($i = 0, \dots, N-1$) is of the Ginzburg–Landau type, cf. (3.8).

Bulk-terrace-step coupling: total atomic-density and configurational force balances. The i -th step, $\Gamma_i(t)$, can be thought of as evolving as a result of the inflow of adatoms from the adjacent upper and lower terraces, $\Omega_i(t)$ and $\Omega_{i-1}(t)$ respectively, and that of bulk atoms from the $(i-1)$ -th film layer, $Q_{i-1}(t)$. Importantly, for a binary substitutional alloy, the net bulk diffusive flux is identically zero, even though the individual species fluxes are not.³⁷ In the absence of edge diffusion, it follows that the total atomic-density balance at the i -th step reduces to

$$\rho^{\text{sites}} V_i = \sum_{k=1}^2 \left\{ J_{i,+}^k + J_{i,-}^k \right\}, \quad (3.39)$$

with ρ^{sites} the constant density of lattice sites (per unit area), and the k -adatom inflows from the upper and lower terraces, $J_{i,-}^k$ and $J_{i,+}^k$ respectively, prescribed by (3.32). If edge diffusion is to be incorporated, the right-hand side of (3.39) needs to be supplemented by the contribution of the edge adatom fluxes,

$$\sum_{k=1}^2 \partial_\varsigma \left(L_{i,s}^k \partial_\varsigma \mu_{i,s}^k \right), \quad (3.40)$$

where ς is the arclength parameter along the $\Gamma_i(t)$, and $L_{i,s}^k = L_s^k(\Theta_i, (\rho_{i-1,b}^{12})^-, \rho_{i-2,b}^{12})$ the non-negative edge atomic mobility, assumed to depend on both the step orientation and chemical composition. Therefore, in the presence of edge atomic diffusion, (3.39) can be rewritten as

$$\rho^{\text{sites}} V_i = \sum_{k=1}^2 \left\{ J_{i,+}^k + J_{i,-}^k + \partial_\varsigma \left(L_{i,s}^k \partial_\varsigma \mu_{i,s}^k \right) \right\} \quad \text{along } \Gamma_i(t). \quad (3.41)$$

The total atomic-density balance is complemented by an interfacial configurational force balance along the i -th step. Roughly, configurational forces are relevant in the presence of non-material defects such as, in the present context, steps on a vicinal surface. More specifically, the working of (i.e., the power expended by) these forces accompanies the evolution of such defects.³⁸ Below is a succinct account of

³⁷This is the so-called substitutional-flux constraint, cf. the discussions by CAHN & LARCHÉ [66] and FRIED & GURTIN [55].

³⁸The early investigations of the role of configurational forces have been variational, cf., e.g., PEACH & KOEHLER [67] on dislocations, HERRING [68] on sintering, and ESHELBY [69, 70, 71, 72] on lattice defects. As such, the variational treatment is contingent upon the a priori specification of constitutive relations and is therefore restricted to particular classes of materials. Moreover, it is not clear whether the variational formalism is not appropriate for dynamical, dissipative settings such as epitaxial growth which occurs away from equilibrium. An alternative approach was developed

how the configurational force balance, when constitutively augmented by Eshelby-type identities, provides a generalization, along the evolving steps, of the classical Gibbs–Thomson relation to the case of multispecies growth away from equilibrium.³⁹

Configurational force balance. Let \mathbf{C}_i and $\mathbf{C}_{i,b}$ be the configurational stress tensors on the i -th terrace $\Omega_i(t)$ and within the i -th film layer $Q_i(t)$ respectively. Furthermore, denote by $\mathbf{c}_{i,s}$ the configurational stress vector along the i -th step, and let $\mathbf{g}_{i,s}$ be the internal configurational force along $\Gamma_i(t)$. The configurational force balance, when localized to the i -th step, yields (cf. CERMELLI & JABBOUR [49], JABBOUR [50], and JABBOUR & VOIGT [60])

$$\underbrace{\mathbf{n}_i \cdot \partial_\zeta \mathbf{c}_{i,s} + \mathbf{n}_i \cdot \mathbf{g}_{i,s}}_{\text{step contribution}} = \underbrace{\mathbf{n}_i \cdot \mathbb{P}_3(\mathbf{C}_{i-1,b})^- \mathbf{n}_i}_{\text{bulk contribution}} - \underbrace{\mathbf{n}_i \cdot \llbracket \mathbf{C} \rrbracket_i \mathbf{n}_i}_{\text{terrace contribution}} \quad \text{along } \Gamma_i(t), \quad (3.42)$$

where $\mathbb{P}_3 := \mathbf{1}_3 - \mathbf{e}_3 \otimes \mathbf{e}_3$ the projection onto the $\{x_1, x_2\}$ -plane and $\mathbf{1}_3$ the three-dimensional identity tensor, and $\llbracket \mathbf{C} \rrbracket_i = \mathbf{C}_{i-1} - \mathbf{C}_i$ the jump in the terrace configurational stress across the i -th step. It can be shown that the bulk configurational stress is given by the following Eshelby-type identity:

$$\begin{aligned} \mathbf{C}_{i,b} = \omega_{i,b} \mathbf{1}_3 - & \left\{ (\nabla \mathbf{u}_i)^\top + \alpha_{i-1} \mathbf{e}_3 \otimes \frac{\mathbf{u}_{i-1} - \mathbf{u}_i}{a} \right\} \mathbf{T}_i \\ & - \epsilon \nabla \rho_{i,b}^{12} \otimes \nabla \rho_{i,b}^{12} - \epsilon \left\{ \alpha_{i-1} \frac{\rho_{i-1,b}^{12} - \rho_{i,b}^{12}}{a} \right\}^2 \mathbf{e}_3 \otimes \mathbf{e}_3 \\ & - \epsilon \left\{ \alpha_{i-1} \frac{\rho_{i-1,b}^{12} - \rho_{i,b}^{12}}{a} \right\} (\nabla \rho_{i,b}^{12} \otimes \mathbf{e}_3 + \mathbf{e}_3 \otimes \nabla \rho_{i,b}^{12}), \end{aligned} \quad (3.43)$$

with \mathbf{T}_i given by (3.13) and

$$\omega_{i,b} := \Psi_{i,b} - \sum_{k=1}^2 \mu_{i,b}^k \rho_{i,b}^k \quad (3.44)$$

the grand canonical potential (per unit area) of the i -th film layer, whereas the terrace configurational stress reduces to:

$$\mathbf{C}_i = \omega_i \mathbb{P}_3, \quad (3.45)$$

where ω_i , the terrace grand canonical potential, is defined by

$$\omega_i := \Psi_i - \sum_{k=1}^2 \mu_i^k \rho_i^k. \quad (3.46)$$

By (3.43)₁ and (3.35), it follows that

$$\mathbf{n}_i \cdot \mathbb{P}_3(\mathbf{C}_{i-1,b})^- \mathbf{n}_i = \omega_{i-1,b} - (\partial_n \rho_{i-1,b}^{12})_i^2, \quad (3.47)$$

independently by HEIDUG & LEHNER [73], TRUSKINOVSKY [74], and ABEYARATNE & KNOWLES [56] who identify the configurational force as the conjugate of the defect velocity and postulate a kinetic relation by which the latter is a thermodynamically compatible function of the former. A different approach is proposed by GURTIN & STRUTHERS [75] and GURTIN [57, 52, 53] who views configurational forces as primitive fields rather than variational constructs, and postulates a balance for these forces distinct from the one that governs their Newtonian counterparts. It is this point of view that we espouse here.

³⁹A more detailed account is to be found in JABBOUR & VOIGT [60].

with $(\partial_n \rho_{i-1,b}^{12})_i := \nabla \rho_{i-1,b}^{12} \cdot \mathbf{n}_i$ the normal-derivative of the relative atomic density within the $(i-1)$ -th layer, ρ_{i-1}^{12} , evaluated along the i -th step, whereas (3.43)₂ yields

$$\mathbf{n}_i \cdot \llbracket \mathbf{C} \rrbracket_i \mathbf{n}_i = \llbracket \omega \rrbracket_i, \quad (3.48)$$

with $\llbracket \omega \rrbracket_i = \omega_{i-1} - \omega_i$ the jump in the terrace grand canonical potential across $\Gamma_i(t)$. Furthermore, letting $\gamma_i = \gamma(\Theta_i)$ denote the Helmholtz free-energy density (per unit length) of the i -th step, it can be shown that consistency with the second law imposes the following Eshelby-type identity:⁴⁰

$$\mathbf{c}_{i,s} = \gamma_i \mathbf{t}_i + \frac{\partial \gamma_i}{\partial \Theta_i} \mathbf{n}_i, \quad (3.49)$$

where \mathbf{t}_i is the unit tangent along $\Gamma_i(t)$ (obtained by rotating \mathbf{n}_i by $\pi/2$ clockwise). Hence, when edge adatom densities are negligible, the step line-tension, the tangential component of the step configurational stress vector, equals its free-energy density. It then follows that

$$\mathbf{n}_i \cdot \partial_\zeta \mathbf{c}_{i,s} = \tilde{\gamma}_{i,s} K_i, \quad (3.50)$$

where $K_i = \partial_\zeta \Theta_i$ is the curvature of the i -th step, and $\tilde{\gamma}_{i,s}$ its stiffness:

$$\tilde{\gamma}_{i,s} := \gamma_{i,s} + \frac{\partial^2 \gamma_{i,s}}{\partial \Theta_i^2}. \quad (3.51)$$

Moreover, we shall show in Section 4 that the constitutive prescription

$$\mathbf{n}_i \cdot \mathbf{g}_{i,s} = -\beta_{i,s} V_i + \sum_{k=1}^2 (\mu_{i,s}^k - \mu_{i-1,b}^k) \rho_{i-1,b}^k + \epsilon (\partial_n \rho_{i-1,b}^{12})^2, \quad (3.52)$$

with $\beta_{i,s} = \beta_{i,s}(\Theta_i, (\rho_{i-1,b}^{12})^-)$ the non-negative kinetic modulus associated with the i -th step, is thermodynamically compatible. Finally, substitution of (3.47), (3.48), (3.50), and (3.52) into the (3.42) yields the following step evolution equation:

$$\beta_{i,s} V_i = \llbracket \omega \rrbracket_i - \Psi_{i-1,b} + \mu_{i,s}^1 \rho_{i-1,b}^1 + \mu_{i,s}^2 \rho_{i-1,b}^2 + \tilde{\gamma}_i K_i, \quad (3.53)$$

which, making use of the lattice constraint

$$\rho_{i-1,b}^1 + \rho_{i-1,b}^2 = \rho^{\text{sites}}$$

and the definition of the relative atomic density

$$\rho_{i-1,b}^1 - \rho_{i-1,b}^2 = \rho_{i-1,b}^{12},$$

reduces to

$$\beta_{i,s} V_i = \llbracket \omega \rrbracket_i - \Psi_{i-1,b} + \frac{1}{2} \mu_{i,s}^1 (\rho^{\text{sites}} + \rho_{i-1,b}^{12}) + \frac{1}{2} \mu_{i,s}^2 (\rho^{\text{sites}} - \rho_{i-1,b}^{12}) + \tilde{\gamma}_i K_i. \quad (3.54)$$

Importantly, following an argument by LARCHÉ & CAHN [65] (cf. also FRIED & GURTIN [55]), we can use the postulated continuity of the relative chemical potential, (3.33), to express the step individual chemical potentials $\mu_{i,s}^1$ and $\mu_{i,s}^2$ in terms of

⁴⁰See Section 4 below.

the (limiting value of the) bulk relative chemical potential. Specifically, assuming for simplicity that local equilibrium holds along the i -th step, i.e., $\beta_{i,s} \equiv 0$, and replacing $\mu_{i,s}^2$ by $\mu_{i,s}^1 - \mu_{i-1,b}^{12}$, (3.54) yields the following identity:

$$\mu_{i,s}^1 = \frac{1}{2}(c_{i-1,b}^{12} - 1)(\mu_{i-1,b}^{12})^- + \frac{1}{\rho_{\text{sites}}} \{\Psi_{i-1,b} - \llbracket \omega \rrbracket_i - \tilde{\gamma}_i K_i\}. \quad (3.55)$$

with $c_{i-1,b}^{12} := \frac{\rho_{i-1,b}^{12}}{\rho_{\text{sites}}} = \frac{\rho_{i-1,b}^1 - \rho_{i-1,b}^2}{\rho_{i-1,b}^1 + \rho_{i-1,b}^2}$ the relative atomic concentration within $Q_{i-1}(t)$. Similarly, we obtain:⁴¹

$$\mu_{i,s}^2 = -\frac{1}{2}(c_{i-1,b}^{12} + 1)(\mu_{i-1,b}^{12})^- + \frac{1}{\rho_{\text{sites}}} \{\Psi_{i-1,b} - \llbracket \omega \rrbracket_i - \tilde{\gamma}_i K_i\}. \quad (3.57)$$

qts. (3.55) and (3.57) generalize the classical Gibbs–Thomson relation (cf., e.g., BALES AND ZANGWILL [8]) to the case of binary-alloy epitaxy.

4. Thermodynamic consistency. In relation to isothermal growth, the first and second laws of thermodynamics—i.e., the energy balance and the entropy inequality, respectively—combine into a single inequality, the dissipation inequality, which asserts that the rate at which the energy associated with a given domain is bounded by the rate at which energy is transported into the domain across its boundary augmented by the power expended by the (external) forces acting on it.

We focus on the i -th step.⁴² Let $\mathcal{R}(t)$ denote an arbitrary, time-dependent sub-curve of $\Gamma_i(t)$, viewed as an interfacial pillbox of infinitesimal thickness, cf. Fig. 4.1. Omitting the superscripts $+$ and $-$ by which we have previously labelled limiting values as the step is approached from the lower or upper terrace, or from within the adjacent film layer, the dissipation inequality, or free-energy imbalance, as it applies to $\mathcal{R}(t)$, reads

$$\frac{d}{dt} \int_{\mathcal{R}(t)} \gamma_{i,s} d\zeta \leq \mathcal{E}(t) + \mathcal{W}(t), \quad (4.1)$$

with $\mathcal{E}(t)$ the energy inflow across $\partial\mathcal{R}(t)$ due to accretive and diffusive atomic trans-

⁴¹The jump in the grand canonical potential encapsulates the contribution of adatom diffusion on the adjacent terraces to the step kinetics. This term is often missing in classical step-flow models but, as shown CERMELLI & JABBOUR [76], there exists a growth regime for which it can lead to novel step-bunching instabilities. The term $\beta_{i,s} V_i$, with $\beta_{i,s}$ a kinetic modulus for the i -th step, represents a dissipative force associated with step motion. In classical step-flow models, this term is typically neglected, i.e., local equilibrium is assumed to hold along the steps. However, as pointed out FRIED & GURTIN [55], this term may be important even for small $\beta_{i,s}$ as long as $\beta_{i,s} L_{i,s}^{\max}$ is large, with $L_{i,s}^{\max} := \max\{L_{i,s}^1, L_{i,s}^2\}$. Finally, for $\beta_{i,s} \equiv 0$, we can rewrite (3.53) as

$$\mu_{i,s}^1 \rho_{i-1,b}^1 + \mu_{i,s}^2 \rho_{i-1,b}^2 = \Psi_{i-1,b} - \tilde{\gamma}_i K_i - \llbracket \omega \rrbracket_i, \quad (3.56)$$

where the right-hand side of (3.56) can be shown to coincide with the variational derivative of the total free energy with respect to variations of the position of the interface, holding the composition fixed, cf. WU [77], NORRIS [78], and FREUND [79].

⁴²The complete treatment, accounting for the adjacent terraces and film layer as well as the substrate, is to be found in JABBOUR & VOIGT [60].

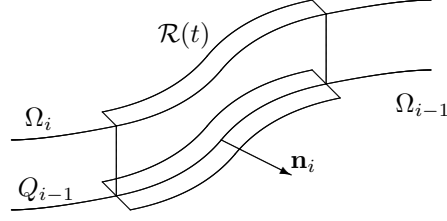


FIG. 4.1. Schematic of an interfacial pillbox along the i -th step. Let $\mathcal{R}(t)$ be an evolving, i.e., time-dependent, subcurve of $\Gamma_i(t)$ whose geometric boundary consists of its two endpoints. Adapting the approach of FRIED & GURTIN [55] to the present setting, i.e., that of step flow on a vicinal surface, we view the interfacial pillbox as encapsulating $\mathcal{R}(t)$ and having an infinitesimal thickness. The pillbox boundary then consists of (i) two curves—in fact the projections of two surfaces of height a —, one with unit normal \mathbf{n}_i and lying on the lower terrace $\Omega_{i-1}(t)$, the other with unit normal $-\mathbf{n}_i(t)$ and lying within the adjacent film layer $Q_{i-1}(t)$ as well as on the upper terrace $\Omega_i(t)$, and (ii) end faces which we identify with the endpoints of $\mathcal{R}_i(t)$.

ports:

$$\begin{aligned} \mathcal{E}(t) := & \underbrace{\sum_{k=1}^2 \int_{\mathcal{R}(t)} \llbracket \mu^k (\mathbf{L}^k \nabla \mu^k \cdot \mathbf{n} + \rho^k V) \rrbracket_i d\varsigma}_{\text{diffusive and accretive energy inflows from upper and lower terraces}} + \underbrace{\sum_{k=1}^2 \int_{\partial \mathcal{R}(t)} \mu_{i,s}^k \mathbf{L}_{i,s}^k \partial_\varsigma \mu_{i,s}^k}_{\text{energy intake due to edge diffusion}} \\ & - \underbrace{\sum_{k=1}^2 \int_{\mathcal{R}(t)} \mu_{i-1,b}^k (\mathbf{L}_{i-1,b}^k \nabla \mu_{i-1,b}^k \cdot \mathbf{n}_i + \rho_{i-1,b}^k V_i) d\varsigma}_{\text{diffusive and accretive energy inflows from adjacent ascending film layer}}, \quad (4.2) \end{aligned}$$

where, since the edge adatom densities are assumed negligible, the accretive intake of energy into $\mathcal{R}(t)$ across its endpoints is ignored, and we have made use of the notation

$$\int_{\partial \mathcal{R}(t)} \varphi := \varphi(\varsigma_1(t), t) - \varphi(\varsigma_0(t), t), \quad (4.3)$$

where $\varphi(\varsigma, t)$ is a smooth, time-dependent field on $\Gamma_i(t)$, and, for $\Gamma_i(t)$ parametrized by $\mathbf{x}_i = \mathbf{x}_i(\varsigma, t)$, $\mathbf{x}(\varsigma_0(t), t)$ and $\mathbf{x}(\varsigma_1(t), t)$ the locations of the endpoints of $\mathcal{R}(t)$ such that $\varsigma_0(t) < \varsigma_1(t)$ for all t ; and $\mathcal{W}(t)$ denotes the power expended by configurational, standard, and microforces on the boundary of the interfacial pillbox:

$$\begin{aligned} \mathcal{W}(t) := & \underbrace{\int_{\mathcal{R}(t)} \llbracket \mathbf{C} \rrbracket_i \mathbf{n}_i \cdot \mathbf{v}_i d\varsigma - \int_{\mathcal{R}(t)} \mathbb{P}_3 \mathbf{C}_{i-1,b} \mathbf{n}_i \cdot \mathbf{v}_i d\varsigma + \int_{\partial \mathcal{R}(t)} \mathbf{c}_{i,s} \cdot \mathbf{v}_{\partial \mathcal{R}(t)}}_{\text{power expended by terrace, bulk, and edge configurational forces}} \\ & - \underbrace{\int_{\mathcal{R}(t)} \mathbb{P}_3 \mathbf{T}_{i-1,b} \mathbf{n}_i \cdot D_t \mathbf{u}_{i-1} d\varsigma}_{\text{standard-traction working}} - \underbrace{\int_{\mathcal{R}(t)} \boldsymbol{\varepsilon}_{i-1,b} \cdot \mathbf{n}_i D_t \rho_{i-1,b}^{12} d\varsigma}_{\text{microforce working}}, \quad (4.4) \end{aligned}$$

where $\mathbb{P}_3 := \mathbf{1} - \mathbf{e}_3 \otimes \mathbf{e}_3$ is the projection of \mathbb{R}^3 onto the plane, $\mathbf{v}_i := \partial_t \mathbf{x}_i(\zeta, t)$ the velocity of the i -th step, and

$$D_t \mathbf{u}_i := \partial_t \mathbf{u}_i + (\nabla \mathbf{u}_i) \mathbf{v}_i$$

and

$$D_t \rho_{i,b}^{12} := \partial_t \rho_{i,b}^{12} + \nabla \rho_{i,b}^{12} \cdot \mathbf{v}_i$$

the time-derivatives of \mathbf{u}_i and $\rho_{i,b}^{12}$ following the evolution of $\Gamma_i(t)$ respectively, and we have made use of the notation

$$\int_{\partial \mathcal{R}(t)} \mathbf{c}_{i,s} \cdot \mathbf{v}_{\partial \mathcal{R}(t)} := \mathbf{c}_{i,s}(\zeta_1(t), t) \dot{\zeta}_1(t) - \mathbf{c}_{i,s}(\zeta_0(t), t) \dot{\zeta}_0(t). \quad (4.5)$$

Importantly, by (3.35), the working of the standard traction that the $(i-1)$ -th film layer exerts on $\mathcal{R}(t)$ vanishes. Now, the species balances along the i -th step read

$$\mathbf{J}_{i,+}^k + \mathbf{J}_{i,-}^k + \partial_\zeta \left(\mathbf{L}_{i,s}^k \partial_\zeta \mu_{i,s}^k \right) - \mathbf{L}_{i-1,b}^k \nabla \mu_{i-1,b}^k \cdot \mathbf{n}_i = \rho_{i-1,b}^k V_i, \quad (4.6)$$

for $k = 1, 2$. Moreover, applying the divergence theorem for line integrals,⁴³ we obtain the identity

$$\int_{\partial \mathcal{R}(t)} \mu_{i,s}^k \mathbf{L}_{i,s}^k \partial_\zeta \mu_{i,s}^k = \int_{\mathcal{R}(t)} \left\{ \mu_{i,s}^k \partial_\zeta (\mathbf{L}_{i,s}^k \partial_\zeta \mu_{i,s}^k) + \mathbf{L}_{i,s}^k (\partial_\zeta \mu_{i,s}^k)^2 \right\} d\zeta. \quad (4.7)$$

Furthermore, appealing to the step atomic-density jump conditions (3.31)_{1,2}, the continuity of the relative chemical potential (3.33), the species equations (4.6), and recalling that the bulk net atomic flux is identically zero for a substitutional alloy, it follows that

$$\begin{aligned} \mathcal{E}(t) = & \underbrace{\sum_{k=1}^2 \int_{\mathcal{R}(t)} \rho_{i-1,b}^k (\mu_{i,s}^k - \mu_{i-1,b}^k) V_i d\zeta}_{\text{energetic contribution due to adatom absorption}} + \underbrace{\sum_{k=1}^2 \int_{\mathcal{R}(t)} \mathbf{L}_{i,s}^k (\partial_\zeta \mu_{i,s}^k)^2 d\zeta}_{\text{energetic contribution via edge diffusion}} \\ & + \underbrace{\sum_{k=1}^2 \int_{\mathcal{R}(t)} \left\{ (\mu_i^k - \mu_{i,s}^k) \mathbf{J}_{i,+}^k + (\mu_{i-1}^k - \mu_{i,s}^k) \mathbf{J}_{i,-}^k \right\} d\zeta}_{\text{energetic contribution due to adatom attachment-detachment}}. \quad (4.8) \end{aligned}$$

In addition, decomposing the step configurational-stress vector according to

$$\mathbf{c}_{i,s} = \sigma_i \mathbf{t}_i + \tau_i \mathbf{n}_i,$$

with σ_i the line tension associated with the i -th step and τ_i the configurational shear, and appealing to the line divergence theorem, the definition of the curvature of the i -th step, $K_i = \partial_\zeta \Theta_i$, the kinematic identity $\partial_\zeta V_i = \dot{\Theta}_i$, and the chain rule, we obtain the following identity:

$$\int_{\partial \mathcal{R}(t)} \mathbf{c}_{i,s} \cdot \mathbf{v}_{\partial \mathcal{R}(t)} = \int_{\mathcal{R}(t)} \left\{ \tau_i \dot{\Theta}_i + (\partial_{\Theta_i} \tau_i) K_i V_i \right\} d\zeta + \int_{\partial \mathcal{R}(t)} \sigma_i \mathbf{v}_{\partial \mathcal{R}(t)} \cdot \mathbf{t}_i, \quad (4.9)$$

⁴³For a smooth (scalar) field φ along the i -th step, the divergence theorem states that $\int_{\mathcal{R}(t)} \partial_\zeta \varphi d\zeta = \int_{\partial \mathcal{R}(t)} \varphi$, with the right-hand side given by (4.3).

where we make use of the notation

$$\int_{\partial\mathcal{R}(t)} \varphi \mathbf{v}_{\partial\mathcal{R}(t)} \cdot \mathbf{t}_i := \varphi(\varsigma_1(t), t) \dot{\varsigma}_1(t) - \varphi(\varsigma_0(t), t) \dot{\varsigma}_0(t).$$

Now, if we appeal to the transport theorem for line integrals,⁴⁴

$$\frac{d}{dt} \int_{\mathcal{R}(t)} \gamma_{i,s} d\varsigma = \int_{\mathcal{R}(t)} \left\{ \overset{\circ}{\gamma}_{i,s} - \gamma_{i,s} K_i V_i \right\} d\varsigma + \int_{\partial\mathcal{R}(t)} \gamma_{i,s} \mathbf{v}_{\partial\mathcal{R}} \cdot \mathbf{t}_i, \quad (4.10)$$

and if we postulate that the dissipation inequality hold irrespective of the choice of parametrization of $\Gamma_i(t)$, and by consequence of the tangential velocities of the endpoints of $\mathcal{R}(t)$, we obtain the identity of the line tension with the step free-energy density:

$$\sigma_i = \gamma_i, \quad i = 1, \dots, N. \quad (4.11)$$

Hence, appealing to (3.42), (4.8), (4.9), (4.10), and (4.11), and recalling that the choice of the subcurve $\mathcal{R}(t)$ is arbitrary, the dissipation inequality (4.1) yields

$$\begin{aligned} \overset{\circ}{\gamma}_i - \tau_i \overset{\circ}{\Theta}_i - \sum_{k=1}^2 L_{i,s}^k (\nabla \mu_{i,s}^k)^2 - \sum_{k=1}^2 (\mu_i^k - \mu_{i,s}^k) J_{i,+}^k - \sum_{k=1}^2 (\mu_{i-1}^k - \mu_{i,s}^k) J_{i,-}^k \\ - \left\{ \sum_{k=1}^2 \rho_{i-1,b}^k (\mu_{i,s}^k - \mu_{i-1,b}^k) + \epsilon (\partial_n \rho_{i-1,b}^{12})^2 - \mathbf{g}_{i,s} \cdot \mathbf{n}_i \right\} V_i \leq 0. \end{aligned} \quad (4.12)$$

Now, we let $\gamma_i = \gamma_i(\Theta_i)$ and require that the dissipation inequality hold for any thermodynamic process. Given that the dependence of the left-hand side of (4.12) on $\overset{\circ}{\Theta}_i$ is linear, the latter can be chosen to violate the dissipation inequality unless its coefficient is identically zero. Hence the step configurational shear has to satisfy

$$\tau_i = \partial_{\Theta_i} \gamma_i \quad \text{for } i \in \{1, \dots, N\}, \quad (4.13)$$

and it is easily seen that the constitutive relations (3.32) and (3.52) are sufficient for (4.12) to hold, granted that the attachment-detachment coefficients, $K_{i,+}^k$ and $K_{i,-}^k$, the edge-adatom mobilities, $L_{i,s}^k$, and the step kinetic modulus, $\beta_{i,s}$, are all non-negative. Finally, the dissipation \mathcal{D}_i along the i -th step reduces to

$$\begin{aligned} \mathcal{D}_i := & \underbrace{\sum_{k=1}^2 L_{i,s}^k (\nabla \mu_{i,s}^k)^2}_{\text{dissipation due to adatom edge diffusion}} + \underbrace{\beta_{i,s} V_i^2}_{\text{dissipation due to adatom absorption into bulk}} \\ & + \underbrace{\sum_{k=1}^2 K_{i,-}^k (\mu_i^k - \mu_{i,s}^k)^2 + \sum_{k=1}^2 K_{i,+}^k (\mu_{i-1}^k - \mu_{i,s}^k)^2}_{\text{dissipation due to adatom attachment-detachment}} \geq 0. \end{aligned} \quad (4.14)$$

⁴⁴Cf., e.g., GURTIN [57].

5. Conclusions. Our goal is a thermodynamically consistent theory for multi-species epitaxy at the nanoscale. For simplicity, we have focused on the binary case. The two main features of the proposed model are (i) the extension of the discrete-continuum BCF formalism and (ii) the derivation of novel boundary conditions at the evolving steps that couple the transport of atoms on the terraces and along the step edges to the bulk atomic diffusion and elasticity. Specifically, we represent the film as a layered nanostructure such that the interfaces that separate adjacent layers are virtual extensions of the terraces of the vicinal surface. Importantly, this layered structure provides a most natural geometric framework within which to capture the atomic exchanges between bulk and surface. Moreover, following GURTIN [57, 54], we postulate separate balances for the configurational and microforces. The former forces accompany the evolution of steps whereas the latter forces are associated with the changes in the bulk relative atomic density viewed as an order parameter for phase separation within the film layers. Finally, we endow the film layers with free energies of the Ginzburg–Landau type and derive sufficient conditions that ensure the compatibility of the constitutively augmented evolution equations with the second law.

The proposed theory should provide an appropriate paradigm for the study of the role of steps in alloy formation and phase segregation during growth. As such, it should pave the way to a better understanding of the formation of nanostructures such as multilayers, two-dimensional stripes, quantum dots, etc. during multicomponent hetero-epitaxy. The stability analysis and numerical implementation of the resulting free-boundary problem are in progress.

Appendix A. Consistency with BCF-type theories for single-species epitaxy.

Here we assume that both film and substrate consist of the same single species which, without loss of generality, we take to be species 1. Accordingly, all fields associated with species 2 are assumed to vanish, e.g., $\rho_i^2 = \mu_i^2 = \mu_{i,s}^2 = 0$, etc. It then follows that the relative atomic density and chemical potential reduce to their counterparts for species 1, $\rho_{i,b}^{12} = \rho_i^1$, $\mu_{i,b}^{12} = \mu_{i,b}^1$, etc. For simplicity, we omit superscripts, with the implicit understanding that all fields and parameters are associated with species 1, e.g., ρ_i refers to ρ_i^1 , the atomic density of adatoms on the first (and only) species on the i -th terrace, etc. Importantly, in the absence of vacancies in the bulk, atomic diffusion is absent from both film and substrate and, correspondingly, bulk atomic densities are fixed, i.e., $\rho_{i,b} = \rho^{\text{sites}}$ and $\rho^{-1,b} = \rho_{-1}^{\text{sites}}$, with $\rho^{\text{sites}} = a\rho_{-1}^{\text{sites}}$, the density of lattice sites (per unit area) a prescribed constant and a the lattice parameter for both film and substrate. Hence the bulk diffusion equations, (3.6) and (3.17), are trivially satisfied. Moreover, since growth is now homo-epitaxial, there is no lattice-parameter mismatch between film and substrate.⁴⁵ Hence, we assume that the displacement within the i -th layer (substrate) is identically zero, $\mathbf{u}_i \equiv \mathbf{0}$ ($\mathbf{u}_{-1} \equiv \mathbf{0}$), and so is the corresponding stress field, $\mathbf{T}_i \equiv \mathbf{0}$ ($\mathbf{T}_{-1} \equiv \mathbf{0}$), i.e., both film and substrate are stress-free.⁴⁶ Therefore, the bulk mechanical-equilibrium conditions, (3.7) and (3.18), hold identically. Finally, in the absence of phase segregation, microforces, defined as forces whose working accompanies variations in the bulk relative atomic density, are extraneous to the formulation of the problem.

⁴⁵We do not consider growth of a single-species film upon a substrate made of another material, e.g., Si on Ge. As discussed in Section 1, such growth is hetero-epitaxial.

⁴⁶For homo-epitaxy, the absence of compositional inhomogeneities in the bulk implies that the solute stress is identically zero.

The PDE's (3.1) now reduce to a single reaction-diffusion equation for the transport, i.e., adsorption-desorption and diffusion, of adatoms on the i -th terrace

$$\partial_t \rho_i - L \Delta \mu_i = F - \gamma \mu_i \quad \text{upon } \Omega_i(t), \quad (\text{A.1})$$

where L , F , and γ are the constant adatom mobility coefficient, deposition flux, and desorption coefficient. Here, as for the multispecies case, the adatom chemical potential is given by

$$\mu_i = \partial_{\rho_i} \Psi_i, \quad (\text{A.2})$$

where, letting $\theta_i := \frac{\rho_i}{\rho_{\text{sites}}}$ denote the adatom coverage density (per unit area) and ω be the energy per interatomic bond, and assuming that the terraces are regular binary solutions with the two species being the adatoms and the open adsorption sites, the terrace free-energy density is prescribed according to:

$$\Psi_i = \Psi(\rho_i) = \Psi(\theta_i) = 4\omega\theta_i(1 - \theta_i) + k_B T \{ \theta_i \ln \theta_i + (1 - \theta_i) \ln(1 - \theta_i) \}. \quad (\text{A.3})$$

Furthermore, omitting the superscripts $+$ and $-$ for the limiting values as the step is approached from the lower and upper adjacent terraces respectively, the supplementary atomic-density jump conditions along the i -th step, (3.31)–(3.32), now reduce to:

$$\left. \begin{aligned} \mathbf{J}_{i,+} &= L \nabla \mu_i \cdot \mathbf{n}_i + \rho_i V_i, \\ \mathbf{J}_{i,-} &= -L \nabla \mu_{i-1} \cdot \mathbf{n}_i - \rho_{i-1} V_i, \end{aligned} \right\} \quad (\text{A.4})$$

where the adatom inflows into the i -th step from the lower and upper adjacent terraces satisfy

$$\left. \begin{aligned} \mathbf{J}_{i,+} &= K_{i,+} \{ \mu_i - \mu_{i,s} \}, \\ \mathbf{J}_{i,-} &= K_{i,-} \{ \mu_{i-1} - \mu_{i,s} \}, \end{aligned} \right\} \quad (\text{A.5})$$

and $K_{i,+} = K_{i,+}(\Theta_i)$ and $K_{i,-} = K_{i,-}(\Theta_i)$ are the adatom attachment-detachment coefficients from the lower and upper terraces respectively, both non-negative.⁴⁷ Furthermore, eqt. (3.33) now takes the form of a continuity condition for the (absolute) chemical potential:

$$\mu_{i-1,b} = \mu_{i,s}, \quad (\text{A.7})$$

whereas the atomic-density equation (3.41) reads as

$$\rho^{\text{sites}} V_i = K_{i,+}(\mu_i - \mu_{i,s}) + K_{i,-}(\mu_{i-1} - \mu_{i,s}) + \partial_\zeta \{ L_{i,s} \partial_\zeta \mu_{i,s} \}, \quad (\text{A.8})$$

with $L_{i,s} = L_s(\Theta_i)$ the non-negative, anisotropic edge-adatom mobility. Finally, the configurational force balance, subject to the assumption of local equilibrium, reduces to

$$\mu_{i,s} = \frac{1}{\rho^{\text{sites}}} \{ \Psi_b - \tilde{\gamma}_i K_i - \llbracket \omega \rrbracket_i \} \quad (\text{A.9})$$

⁴⁷As discussed in footnote 34, if the i -th step acts as a perfect sink of adatoms, then the boundary conditions (A.4) are replaced by their so-called thermodynamic counterparts, i.e.,

$$\mu_i = \mu_{i,s} = \mu_{i-1}. \quad (\text{A.6})$$

with Ψ_b the constant bulk free-energy density (per unit area) and $\tilde{\gamma}_i := \gamma(\Theta_i) + \gamma''(\Theta_i)$ the stiffness of the i -th step.

Now, let ρ_i^{eq} denote the adatom equilibrium density along the i -th step. Following CERMELLI & JABBOUR [49], we expand the terrace chemical potential about ρ_i^{eq} :

$$\mu_i = \mu_i(\rho_i^{\text{eq}}) + \partial_{\rho_i} \mu_i(\rho_i^{\text{eq}}) \{\rho_i - \rho_i^{\text{eq}}\} + \cdots, \quad (\text{A.10})$$

and, appealing to (A.2) and the definition of the terrace grand canonical potential, $\omega_i := \Psi_i - \mu_i \rho_i$, we also arrive at

$$\omega_i = \omega_i(\rho_i^{\text{eq}}) + \rho_i^{\text{eq}} \partial_{\rho_i} \mu_i(\rho_i^{\text{eq}}) \{\rho_i - \rho_i^{\text{eq}}\} + \cdots. \quad (\text{A.11})$$

Thus, by (A.5) and (A.9), it follows that

$$J_{i,+} \sim M_{i,+} \left\{ \rho_i - \rho_i^{\text{eq}} + \frac{\tilde{\gamma}_i}{\rho_{\text{sites}} \partial_{\rho_i} \mu_i(\rho_i^{\text{eq}})} K_i + \frac{\rho_i^{\text{eq}}}{\rho_{\text{sites}}} \llbracket \rho_i - \rho_i^{\text{eq}} \rrbracket_i \right\}, \quad (\text{A.12})$$

with $M_{i,+} := K_{i,+} \partial_{\rho_i} \mu_i(\rho_i^{\text{eq}})$, and

$$J_{i,-} \sim M_{i,-} \left\{ \rho_{i-1} - \rho_i^{\text{eq}} + \frac{\tilde{\gamma}_i}{\rho_{\text{sites}} \partial_{\rho_i} \mu_i(\rho_i^{\text{eq}})} K_i + \frac{\rho_i^{\text{eq}}}{\rho_{\text{sites}}} \llbracket \rho_{i-1} - \rho_i^{\text{eq}} \rrbracket_i \right\}, \quad (\text{A.13})$$

with $M_{i,-} := K_{i,-} \partial_{\rho_i} \mu_i(\rho_i^{\text{eq}})$. Therefore, if we further assume that $\rho_i^{\text{eq}} \ll \rho_{\text{sites}}$, the terms $\frac{\rho_i^{\text{eq}}}{\rho_{\text{sites}}} \llbracket \rho_i - \rho_i^{\text{eq}} \rrbracket_i$ and $\frac{\rho_i^{\text{eq}}}{\rho_{\text{sites}}} \llbracket \rho_{i-1} - \rho_i^{\text{eq}} \rrbracket_i$ become negligible. Hence, in the limit $\frac{\rho_i^{\text{eq}}}{\rho_{\text{sites}}} \rightarrow 0$, the approximate free-boundary problem becomes of the BCF type. Specifically, eqt. (A.1) reduces to

$$\partial_t \rho_i - D_i \Delta \rho_i = F_i - \lambda_i \rho_i, \quad (\text{A.14})$$

with $D_i := L \partial_{\rho_i} \mu_i(\rho_i^{\text{eq}})$, $F_i := F - \gamma \{\mu_i(\rho_i^{\text{eq}}) - \rho_i^{\text{eq}} \partial_{\rho_i} \mu_i(\rho_i^{\text{eq}})\}$, and $\lambda_i := \gamma \partial_{\rho_i} \mu_i(\rho_i^{\text{eq}})$, whereas the step jump conditions (A.4)–(A.5) take the form

$$D_i \nabla \rho_i \cdot \mathbf{n}_i + \rho_i V_i = M_{i,+} \left\{ \rho_i - \rho_i^{\text{eq}} + \frac{\tilde{\gamma}_i}{\rho_{\text{sites}} \partial_{\rho_i} \mu_i(\rho_i^{\text{eq}})} K_i \right\} \quad (\text{A.15})$$

and

$$-D_i \nabla \rho_{i-1} \cdot \mathbf{n}_i - \rho_{i-1} V_i = M_{i,-} \left\{ \rho_{i-1} - \rho_i^{\text{eq}} + \frac{\tilde{\gamma}_i}{\rho_{\text{sites}} \partial_{\rho_i} \mu_i(\rho_i^{\text{eq}})} K_i \right\}. \quad (\text{A.16})$$

Moreover, eqt. (A.9) is approximated by

$$\mu_{i,s} = \mu_{\text{eq}} - \frac{\tilde{\gamma}_i}{\rho_{\text{sites}}} K_i, \quad (\text{A.17})$$

where $\mu_{\text{eq}} := \frac{\Psi_b}{\rho_{\text{sites}}}$. Consequently, defining $D_{i,s} := \frac{L_{i,s}}{\rho_{\text{sites}}}$, eqt. (A.8) takes the form

$$\begin{aligned} \rho_{\text{sites}} V_i &= M_{i,+} \left\{ \rho_i - \rho_i^{\text{eq}} + \frac{\tilde{\gamma}_i}{\rho_{\text{sites}} \partial_{\rho_i} \mu_i(\rho_i^{\text{eq}})} K_i \right\} \\ &+ M_{i,-} \left\{ \rho_{i-1} - \rho_i^{\text{eq}} + \frac{\tilde{\gamma}_i}{\rho_{\text{sites}} \partial_{\rho_i} \mu_i(\rho_i^{\text{eq}})} K_i \right\} - \partial_\zeta \{D_{i,s} \partial_\zeta (\tilde{\gamma}_i K_i)\}. \end{aligned} \quad (\text{A.18})$$

Thus we have obtained the classical BCF model, as described in , e.g., KRUG [9] and PIERRE-LOUIS [11].⁴⁸

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⁴⁸Specifically, a term-by-term comparison with eqts. (3), (5), and (6) of BALES & ZANGWILL [8] yields complete agreement between the approximate boundary conditions derived above, (A.15) and (A.16), and their boundary conditions, granted that our sign convention for the step curvature is opposite to that chosen by these authors and ρ_i^{eq} is given by:

$$\partial_{\rho_i} \mu_i(\rho_i^{\text{eq}}) = \frac{k_B T}{\rho_i^{\text{eq}}}. \quad (\text{A.19})$$

Appealing to (A.3) and (A.2), a straightforward calculation reduces (A.19) to

$$\theta_i^{\text{eq}} = 1 - \frac{k_B T}{8\omega}, \quad (\text{A.20})$$

with $\theta_i^{\text{eq}} := \frac{\rho_i^{\text{eq}}}{\rho_{\text{sites}}}$ the equilibrium adatom coverage on the i -th terrace.

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