Boundary Conditions for Burton–Cabrera–Frank Type Step-Flow Models: Coarse-Graining of Discrete 2D Deposition-Diffusion Equations

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Keywords
step-flow, epitaxial growth, vicinal surfaces, terrace and edge diffusion, deposition-diffusion equations, attachment barrier, Ehrlich–Schwoebel barrier, kinetic coefficients

Disciplines
Mathematics | Physical Chemistry | Statistical, Nonlinear, and Soft Matter Physics

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BOUNDARY CONDITIONS FOR BURTON–CABRERA–FRANK TYPE STEP-FLOW MODELS: COARSE-GRANING OF DISCRETE 2D DEPOSITION-DIFFUSION EQUATIONS∗

DAVID M. ACKERMAN† AND J. W. EVANS‡

Abstract. We analyze discrete two-dimensional (2D) deposition-diffusion equations for the density of adatoms deposited at a periodic array of adsorption sites on a vicinal crystalline surface with kinked steps. Our analysis provides insight into the appropriate boundary conditions (BC) at steps for a coarse-grained Burton–Cabra–Frank (BCF) type treatment involving continuum 2D deposition-diffusion equations. Such a BCF type treatment should describe step flow on vicinal surfaces under nonequilibrium growth conditions. We focus on cases where there is no additional activation barrier inhibiting to attachment at steps beyond that for terrace diffusion. Then, the classical BCF treatment simply imposes a Dirichlet BC equating the limiting value of the terrace adatom density to its equilibrium value at the step edge. Our analysis replaces this BC with one incorporating finite kinetic coefficients, $K_\pm$, measuring inhibited diffusion-limited attachment at kinks. We determine the dependence of $K_\pm$ on key parameters such as the kink separation and terrace width, and on the width of nearby terraces. Our formulation provides a framework within which to describe step pairing phenomena observed on so-called AB-vicinal surfaces without attachment barriers, a feature not captured by the classical BCF treatment.

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1. Introduction. Growth, erosion, and relaxation of crystalline surfaces are often characterized in terms of the motion of steps separating adjacent terraces with a height difference of a single atomic layer [1, 2, 3, 4]. In a detailed discrete atomistic picture of these processes [3, 4], atoms are deposited or removed from the surface. The resulting adatoms or advacancies diffuse across terraces on the surface by hopping between adjacent adsorption sites which form a periodic array or lattice. Potentially, there is also transport of these adspecies between different layers. When the adspecies reach and attach to steps, they can typically diffuse along steps and become incorporated into these steps at kink sites. They can also possibly detach from step edges. These processes together induce the motion of steps. It is natural to coarse-grain this detailed atomistic picture to achieve a so-called continuum step-dynamics picture in which steps are regarded as continuous curves [1, 2, 5, 6]. Their smooth motion is determined by solving continuum diffusion equations on the terraces including an appropriate deposition or erosion driving term and with suitable boundary conditions (BC) at steps. The local velocity of the step is determined largely from the net diffusive flux of atoms to the step. Such equations are referred to as “deposition-diffusion
equations” in this paper. Coarse-graining of atomistic models can potentially enable more efficient computational modeling, and will ideally lead to a deeper or more fundamental understanding of the evolution of surface morphologies. Below, we just use the language of deposition rather than erosion, so that the adspecies are deposited adatoms.

A classic 1951 continuum treatment of Burton, Cabrera, and Frank [7] (BCF) assumed that steps were ideal sources and sinks of adatoms, so that the adatom density on the terraces always approached its local equilibrium value at these steps. In other words, this treatment imposed a simple Dirichlet BC equating the adatoms density at steps to its equilibrium value. Such a situation is generally assumed to apply if there is no additional activation barrier for diffusing adatoms to attach to steps beyond that for terrace diffusion. The current contribution focuses on this case of no attachment barrier. Subsequent refinements of this classic treatment initiated by Chernov accounted for inhibited attachment at step edges [8, 9], and other extensions incorporated partial transparency or permeability of steps [10]. These various refinements lead to BCs with a more complex form involving kinetic coefficients, $K_\pm$, the magnitude of which reflects the ease of attachment to steps, and also involving a permeability coefficient, $P$. See section 2 for a more detailed description. Within this more general framework, the BC in the classical BCF theory can be regarded as corresponding to the choice $K_\pm = \infty$.

Vicinal surfaces present a special, simple terrace-step staircase morphology with an array of parallel steps. This simple morphology provides a natural testing ground to assess various formulations of step dynamics during deposition where the entire step train advances (so-called step flow). Depending on the details of the system, this moving step train can be subject to step pairing, bunching, or meandering instabilities [1, 2, 3, 6]. Of some relevance here is the existence of a specific subclass of what have been called AB-vicinal surfaces which present two distinct types of alternating steps [11]. If these surfaces are stable, then the two types of steps have equal chemical potentials and therefore equal equilibrium adatom densities. Thus, the classical BCF treatment (for no attachment barrier) would impose identical Dirichlet BCs at both types of steps implying equal velocities of all steps for a perfect staircase.

Recently, there has been considerable interest in assessing the validity of BCF type BCs, particularly in the far-from-equilibrium regime realized under conditions of “rapid” growth or erosion [12, 13, 14, 15, 16, 17]. Our focus is also on the validity of BCF type formulations. Our motivation comes from the observation of step pairing in a simple anisotropic solid-on-solid (SOS) model for AB-vicinal surfaces with no attachment barrier [18], behavior which is not described in the classical BCF treatment (as noted just above). Differing from other recent studies [12, 13, 14, 15, 16, 17] described in section 2, our strategy is to develop a discrete two-dimensional (2D) deposition-diffusion equation formulation with which to describe and analyze such behavior. The output is effective kinetic coefficients which can provide input to a coarse-grained BCF formulation with generalized Chernov-type BCs (rather than the classical Dirichlet BC). These coefficients are finite despite the absence of an attachment barrier, and depend on kink separation, thereby elucidating the above-mentioned step pairing phenomena. The inadequacy of the classical BCF formulation can be understood since it implicitly assumes high kink densities (i.e., large terrace widths relative to the typical separation between kinks), whereas step pairing behavior considered here only occurs for limited terrace widths (relative to kink separation).
In section 2, we review the generalized BCF theory by Chernov [8], and also other theories and strategies for description and analysis of step dynamics. In section 3, we briefly describe behavior of an atomistic anisotropic SOS model for AB-vicinal surfaces with no attachment barriers but which displays step pairing contrasting predictions of the classical BCF theory. Then, in section 4, we present our new modeling strategy developing a discrete 2D deposition-diffusion equation model and define relevant kinetic coefficients. Next, in section 5, we analyze in detail the case excluding interlayer transport (i.e., with an infinite barrier to attach to descending steps), but with no barrier to attach to ascending steps. The case where there is no barrier to attach to either ascending or descending steps is analyzed for uniform vicinal surface in section 6. More complex cases with zero attachment barriers are analyzed in section 7, and more general cases with finite attachment barriers are discussed in section 8. A summary is provided in section 9.

2. Step dynamics.

2.1. Traditional (generalized) BCF formulation. The description of step motion during adatom deposition is usually based on quasi-steady-state solutions for the adatom density per unit area, $n(x, t)$ and lateral position $x$ and time $t$. This density satisfies the continuum deposition-diffusion equation [1, 3, 4, 5, 6, 7]

$$\frac{\partial}{\partial t} n(x, t) = F + D \nabla^2 n(x, t) \approx 0. \quad (1)$$

Here, $F$ is the deposition flux per unit area, and $D$ is the terrace diffusion coefficient for adatoms. The density $n(x, t)$ is taken to satisfy BCs at a step edge of the form [7, 8, 9, 10]

$$\pm D \nabla_n n|_{\pm} = K_{\pm} (n_{\pm} - n_{eq}) + P (n_{\pm} - n_{\mp}) (= J_{\pm}), \quad (2)$$

ignoring convection terms given that steps move slowly on the time scale of adatom density relaxation. Here, $\nabla_n$ denotes the normal derivative to the step edge (in the descending direction), and $n_{eq}$ denotes the equilibrium density of the diffusing species. Also $\pm$ indicates the limiting values of various quantities approaching the step edge, where $+$ refers to the lower terrace, and $-$ refers to the upper terrace. See Figure 1. $K_{\pm}$ and $P$ are kinetic coefficients described below.

The expressions in (2) represent the diffusion fluxes, $J_{\pm}$, of adatoms reaching the step edge from the lower (+) and upper (−) terrace, and the step velocity for straight steps is given by $V = J_+ + J_-$. The first term on the right-hand side corresponds to attachment at steps where $K_{\pm}$ are the associated kinetic coefficients [8, 9]. Thus, $K_+$ corresponds to intralayer attachment at ascending steps. $K_-$ corresponds to downward interlayer attachment involving transport over descending steps. The second term on the right-hand side corresponds to transport across the step where $P$ is the step permeability [10]. Rather than being a relation derived from a class of atomistic models, (2) is usually thought of as a defining relation for the kinetic coefficients.

It is instructive to write $K_{\pm} = D/L_{\pm}$, where $L_{\pm}$ are the corresponding attachment lengths. These reflect any additional energy barriers, $\delta_{\pm}$, to attachment at step edges, where $\delta_-$ corresponds to the Ehrlich-Schwoebel (ES) step edge barrier inhibiting downward transport over descending steps [3, 4, 9]. Below, we let “a” denote the surface lattice constant, and $\beta = 1/(k_B T)$ denotes the inverse temperature for surface temperature $T$ and Boltzmann constant $k_B$. Then, traditional formulations typically assign either $L_{\pm} = a \exp(\beta \delta_{\pm}) - 1$ or $L_{\pm} = a \exp(\beta \delta_{\pm})$ [3, 4]. See Appendices A and B. In the case of facile attachment at steps (i.e., $\delta_{\pm} = 0$), the first formulation on
Fig. 1. Schematic of the generalized BCF BCs with total diffusion fluxes \( J_+ = K_+ (n_+ - n_{eq}) + P(n_+ - n_-) \) and \( J_- = K_- (n_- - n_{eq}) + P(n_- - n_+) \) reaching the ascending and descending steps, respectively. Also \( J_p = P(n_- - n_+) \) denotes the flux across the step due to permeability.

which we focus yields \( K_\pm / D = \infty \) or \( L_\pm = 0 \) which recovers classical BCF Dirichlet BC \( n = n_{eq} \). The second yields \( K_\pm / D = 1 / a \) or \( L_\pm = a \) for \( \delta_\pm = 0 \). In the case of an infinite ES barrier precluding interlayer transport, clearly one has that \( K_- = 0 \) and \( P = 0 \) (i.e., the step is impermeable). With finite \( \delta_\pm \), there is no reason to preclude the assignment \( P > 0 \), and for some systems this seems key to describing observed behavior [19]. For the models considered here when the ES barrier is not finite (and usually zero), one expects physically that the steps are permeable (\( P > 0 \)).

Determination of \textit{step velocities}, \( V \), requires solving the above boundary value problems to determine the fluxes, \( J_\pm \). If \( P > 0 \), then the behavior on all terraces is coupled. The case of most relevance here is where the \textit{permeability term drops out of} (2), either because \( P = 0 \) or because \( n_+ = n_- \). Then, the boundary value problem for each terrace is uncoupled from the rest, and one needs only solve these for terraces adjacent to a step to determine the step velocity. For parallel straight steps, the analysis is simple since the steady-state solution of (1) is a parabolic profile. For a single terrace of width \( W \), let \( K_l = D / L_l \) and \( K_r = D / L_r \) denote the K-values for the left (ascending) and right (descending) step, respectively, and \( J_l \) and \( J_r \) the corresponding fluxes. Then, one has that [4]

\[
J_l + J_r = FW \quad \text{and} \quad J_l / (J_l + J_r) = \left[ \frac{1}{2} + L_r / W \right] / [1 + L_l / W + L_r / W] (= P). \tag{3}
\]

The result for the sum of the fluxes follows trivially from mass conservation. We let \( P_l \) (\( P_r \)) denote the fraction of this flux reaching the left (right) step. Then, the expression for \( P_r \) simply follows from that above for \( P_l \) after interchanging the labels \( l \) and \( r \), and one has that \( P_l + P_r = 1 \). From (3), it is clear that knowledge of the K-values, or the corresponding attachment lengths, and the terrace width, \( W \), allows evaluation of the fluxes and thus the step velocities. For completeness, we note that the value of excess adatom density, \( \delta_{n_l} = n - n_{eq} \), at the left and right steps can be determined from \( K_l \delta_{n_l} = J_l \) and \( K_r \delta_{n_r} = J_r \), respectively.

Finally, we emphasize one consequence of (3): any assignment of attachment lengths far below the terrace widths corresponds to “large” K-values or facile attachment, and yields similar behavior for step dynamics to the classical BCF Dirichlet BC. One should regard \( K_\pm / D = O(1 / a) \) as “large.”
2.2. Other established formulations and refinements. A well-established formulation prominent in the liquid-phase crystal growth community is based on the observation that step motion derives from incorporation of atoms at kinks and the resulting motion of those kinks [20, 21]. A simple geometric argument implies that the step velocity, \( V \), satisfies \( V \propto v_{\text{kink}}/L \), where \( L \) is the typical kink separation and \( v_{\text{kink}} \) is the kink velocity along the step. Typically, it is assumed that attachment to kinks is strongly inhibited by a kink attachment barrier, \( \delta_{\text{kink}} \). Then, one has that \( v_{\text{kink}} \sim \exp(-\beta\delta_{\text{kink}})(n - n_{\text{eq}}) \). This, in turn, implies a step kinetic coefficient of the form \( K \sim \exp(-\beta\delta_{\text{kink}})/L \). This formulation will not apply to the models of interest here where there are no attachment barriers of any type. However, it is appropriate to note that our analysis will also produce a dependence of \( K \) on \( L \) (but of a different form).

Within the above picture (which again does not apply for our models), the mean kink separation or density is a key factor in determining step propagation, with higher kink densities implying higher propagation velocities. Thus, one should ask what determines the value of this kink density. For higher temperatures, \( T \), thermal fluctuations of the steps will spontaneously produce a high density of kinks which will presumably be close to their equilibrium value. However, for lower \( T \) (or high kink energy), kinks may be rare. Then, the kink density during deposition and step flow may be determined by kinetic factors associated with the one-dimensional (1D) nucleation of new rows of atoms on the step. A corresponding kinetic theory has been developed by Voronkov [22] and others [21]. Such kinetic formulations are the precursors of more recent detailed treatments of nonequilibrium step flow described below in section 2.3.

All of the above formulations apply for the propagation of straight steps. Step evolution in situations with curved steps, e.g., growth of 2D islands, is often analyzed by decomposing the step velocity into two components. One component comes from diffusion-mediated attachment-detachment of atoms from or to the terrace described above by (2), and the second from diffusion along the step edge. In general, the island growth shape [3, 4] is determined by interplay between (i) a Mullins–Sekerka type instability associated with diffusion-limited aggregation of terrace adatoms, and (ii) relaxation of the shape of the growing island due to edge diffusion. Both depend sensitively on the local curvature, and the latter depends on the orientation of the step edge. The edge diffusion flux controlling relaxation can be dominated by a nonequilibrium component (proportional to the local aggregation flux) rather than by the traditional Mullins-type step edge flux which is determined by the gradient in curvature [3, 4]. Heuristic forms have been proposed for the nonequilibrium edge flux [23], but rigorous analysis is limited [24].

Finally, we note that the step velocity is given by the net flux of attachment of atoms at the step edge accounting for all attachment pathways. In addition to contributions from diffusion across adjacent terraces and along the step edge, there is the possibility of direct deposition at the step edge. Of course, this contribution will be minor for broad terraces of many lattice constants. Also, relative to traditional atomistic models based on a simple-cubic crystal structure (SOS models), sites at the step edge actually directly capture more depositing atoms than terrace sites for realistic face-centered or body-centered cubic structures due to “downward funneling” of atoms deposited right at the step edge [25]. One can readily incorporate this effect into step dynamics or discrete models by augmenting the direct deposition flux at step edge sites. Correct accounting for this feature is particularly important for predictions of slope selection during mound formation [26].
2.3. Kinetic terrace-step-kink models. One general strategy utilized in recent analyses of nonequilibrium step dynamics starts with a terrace-step-kink picture of the surface [2, 7] and develops separately mean-field diffusion equations for the density of terrace adatoms and for that of edge adatoms, as well as a mean-field convection equation for the density of kinks [12, 13, 14, 15, 16, 17]. Constitutive relations are also required for various quantities; e.g., step attachment and detachment fluxes are calculated in terms of the limiting value of the terrace adatom density at the step edge and the actual nonequilibrium edge atom density. Development of this formulation is simplest for step orientations with low kink densities [12], but has been extended to other step orientations [15, 16]. The latter development is related to a key component of this paper, i.e., consideration of the dependence of the kinetic coefficient on kink density (noting that kink density is simply related to step orientation).

The focus of these studies has for the most part been in determining key properties of nontrivial nonequilibrium steady-state associated with step flow such as the kink density [12, 13, 14, 15, 16]. However, the work of Margetis and Caflisch (MC) [17] also presented results for kinetic coefficients defined by the relation (2), connecting more closely with our focus. MC utilized a perturbation analysis for the regime of small Peclet number (which is inversely proportional to the edge diffusion rate). The study by MC is distinct from but complementary to our own work: MC regards attachment fluxes or adatom densities approaching the step as input parameters and solves for the nonequilibrium steady-state step geometry including kink density. In contrast, we will specify the surface geometry (including the kink distribution along steps) as input and solve the corresponding diffusion-diffusion equation to determine kinetic coefficients.

Interestingly, MC also introduces an effective nonequilibrium stiffness from a perturbation analysis of step flow for slightly curved steps. An analogy is exploited with the equilibrium Gibbs–Thomson relation which relates the equilibrium adatom density for curved steps to step stiffness. Usually stiffness of steps (or more generally of interfaces) is assessed from interface fluctuations. For equilibrated interfaces, the fluctuation amplitude is inversely proportional to stiffness and completely independent of interface mobility [2]. In contrast, the lack of a fluctuation-dissipation relation for general nonequilibrium systems introduces some ambiguity since the mobility no longer factors out of expressions for the fluctuation amplitudes [27]. However, the approach of [17] avoids this ambiguity.

2.4. Discrete lattice-based deposition-diffusion models. An alternative class of strategies to assess appropriate BCs in a BCF formulation for step flow might be based on discrete deposition-diffusion equations describing the adatom density at a discrete periodic array of adsorption sites on stepped crystalline surfaces. A few previous studies have examined the steady-state solutions of the 1D version of these equations for step flow on vicinal surfaces [3, 4, 28]. Coarse-graining then allows derivation of BCs of the type (2), as discussed further in Appendix B. However, such 1D models must necessarily describe in an average or effective fashion the complex structure of steps in physical 2D surface systems where steps have both kink and ledge sites [29].

Thus, in the current study, we are motivated to analyze models based on the steady-state solutions of discrete 2D deposition-diffusion equations which explicitly incorporate the kink and ledge site structure of steps on a vicinal surface. All the details of our model are described in section 4.1. Certainly our modeling is still somewhat idealized in that it incorporates a simple frozen step geometry. However, it
still provides new insights into nonequilibrium step flow, thereby supplementing the alternative modeling strategies of section 2.3. A goal of these studies is to obtain appropriate BCs for continuum step-dynamics models which are regarded as deriving from coarse-graining of the discrete models over length scales larger than the typical kink separation. A specific aim is to characterize the dependence of the effective kinetic coefficients \( K_{\pm} \) on the microscopic parameters in the discrete model, particularly on the mean kink separation.

3. AB-vicinal surfaces and nonequilibrium step pairing. Perhaps the most familiar example of an AB-vicinal surface [11], and one with immense technological significance, is that of vicinal Si(100) [30, 31]. A dimer-row reconstruction of the Si(100) surface, together with an alternation of the direction of the dimer rows on adjacent terraces, leads to alternating so-called \( S_A \) and \( S_B \) type step types. \( S_B \) steps have low stiffness and thus meander greatly with a high kink density. \( S_A \) steps are stiff and relatively straight with a low kink density. Step pairing has been observed experimentally during deposition on a vicinal Si(100) surface with \( S_B \) steps initially moving faster than \( S_A \) steps. Faster propagation of the more kinked \( S_B \) step has been rationalized with the framework of the model for inhibited kink attachment described in section 2.2, refined by ideas of Voronkov to account for kinetic contributions to the (low) kink density on \( S_A \) steps, and also accounting for anisotropic terrace diffusion [21]. It should be emphasized that this is a particularly complex system due to the surface reconstruction. In addition to the features above, attachment and detachment at steps effectively occurs in units larger than atoms (dimers or dimer pairs) [30]. Thus, precise atomistic level modeling is difficult. For this reason, sometimes a heuristic approach is adopted of simply assigning distinct kinetic coefficients to \( S_A \) and \( S_B \) steps, the coefficient for \( S_B \) steps being larger and reflecting higher “accommodation” or “stickiness” at \( S_B \) steps [32]. A similar heuristic approach has been adopted in analyses of island formation during Si(100) homoepitaxy [33, 34].

Another example of an AB-vicinal surface, structurally equivalent to Si(100), is provided by vicinal Ge(100) surfaces. A rather different realization is provided by surfaces of hexagonal close-packed (hcp) metal crystals vicinal in the principal direction to the basal plane [11], where close-packed steps alternate between [100]- and [111]-microfaceted structures.

However, our purpose here is to provide a fundamental understanding of step dynamics. Thus, rather than considering a detailed realistic model for a specific system such as Si(100), it is more instructive to consider a simpler generic model. To this end, we consider a simple anisotropic SOS model as developed in [18] which includes random deposition at rate \( F \) per site, isotropic terrace diffusion with barrier \( E_d \), and no attachment barriers at steps. There are attractive anisotropic interactions between deposited atoms on nearest-neighbor (NN) adsorption sites. These attractions lead to a thermodynamic preference for aggregation of adatoms with steps or into islands. Specifically, the model incorporates stronger attractive NN interactions \( \phi_s > 0 \) in one direction and weaker NN attractions \( \phi_w > 0 \) in the orthogonal direction. Furthermore, these directions alternate between adjacent terraces on a vicinal surface. Activation barriers for either intralayer or interlayer hopping to NN empty sites are chosen to have the form \( E_{act} = E_d + n_s \phi_s + n_w \phi_w \), where \( n_s \) (\( n_w \)) is the number of strongly (weakly) bonded neighbors in the same layer before hopping. Hop rates are given by \( h = \nu \exp[-\beta E_{act}] \), where again \( \beta = 1/(k_B T) \). As a result of anisotropic interactions, the vicinal surface displays two types of steps, alternating between straight or stiff (which we denote type-A), and wandering or meandering (which we denote type-B).
For B-type meandering steps, the strong bonding is orthogonal to the step, so kink creation is controlled weak bonding which leads to a high density of kinks [2]. For A-type stiff steps, the opposite is true.

Model behavior as determined from kinetic Monte Carlo (kMC) simulations is shown in Figure 2. Before deposition, on average the two different types of steps are equally spaced. When deposition is initiated, step pairing occurs, the meandering B-type steps initially moving faster than the A-type stiff steps. However, both types of steps have the same equilibrium density, $n_{eq} = \exp[-\beta \phi_b]$, where $\phi_b = \phi_s + \phi_w$, and thus should advance with the same velocity according to the traditional BCF Dirchlet BC. Thus, the observed pairing is a nonequilibrium phenomenon, which has been described previously only qualitatively in terms of differences in “accommodation” or “stickiness” of the two types of steps [18]. The current work will provide a more precise and quantitative formulation.

![Image](https://www.siam.org/journals/ojsa.php)

**Fig. 2.** Images ($200 \times 200$ sites) from our KMC simulation of the anisotropic SOS model for step flow on an AB-vicinal surface with higher terraces on the right: (a) structure of the equilibrated surface (before deposition) with on-average equal spaced steps and alternating A-type stiff and B-type meandering steps; (b) structure after deposition of $\sim 0.6$ layers of atoms. Parameter choices: $\beta \phi_s = 7.25$, $\beta \phi_w = 2.90$, and $\nu/F = 10^8$.

4. Discrete 2D deposition-diffusion equations for vicinal surfaces.

4.1. Model specification. Guided by the anisotropic SOS model described in section 3, we first consider an idealized 2D deposition-diffusion equation model for deposition on a perfect vicinal surface where all terraces have a width of $W$ sites. Kinks are periodically distributed along each step edge with a separation of $L$ lattice constants. Also kinks on different steps are aligned in the direction orthogonal to the steps. Due to periodicity both orthogonal to and parallel to the steps, we need only analyze behavior of the adatom density in an $L \times W$ site “rectangular unit cell” on a single terrace between adjacent kink sites. We label sites in this unit cell by $(i,j)$, where $1 \leq i \leq L$ and $1 \leq j \leq W$. Step edge sites $(i,1)$ correspond to those at the bottom of an ascending step, where $(1,1)$ is regarded as a kink site which acts as a source and sink for adatoms. Sites $(i,W)$ correspond to those at the upper edge of a descending step. See Figure 3. The adatom density at site $(i,j)$ is denoted by $n(i,j)$, where the density at the kink site is fixed at a constant value of unity; i.e., $n(1,1) = 1$. 

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Fig. 3. Schematic of discrete 2D deposition-diffusion model for perfect vicinal surface. We show adsorption sites in a $L \times W$ rectangular unit cell together with nearby surrounding sites, and also indicate kink sites. Rates of various hopping processes (and of deposition) are also indicated.

Next, we describe the energetics and dynamics of the model also illustrated in Figure 3 where again $\beta = 1/(k_B T)$. Atoms are deposited at rate $F$ per site. Given our interest in anisotropic systems, we allow for direction-dependence of the bonding of adatoms to step edge atoms. Edge adatoms at sites $(i,1)$ with $1 < i \leq L$ adjacent to the ascending step are regarded as bonded to the step edge atoms via an NN attraction of strength $\phi^\perp > 0$. In addition, these edge adatoms (with $j=1$) upon reaching the kink sites are regarded as acquiring additional bonding of strength $\phi^\parallel > 0$. A terrace atom at site $(2,1)$ upon directly reaching the kink site $(1,1)$ is regarded as acquiring additional bonding of strength $\phi_b = \phi^\perp + \phi^\parallel > 0$. Thus, the total strength of bonding for adatoms at kink sites is consistently given by $\phi_b$. Edge adatoms at sites $(i,W)$ adjacent to the descending step do not have any lateral bonding.

Hopping of adatoms from terraces sites $(i,j)$ to other sites on the same terrace typically occurs at rate $h$ for $2 \leq j \leq W$. The only exception is for hopping from site $(i,2)$ to $(i,1)$, which corresponds to attaching to an ascending step, and where the rate may be reduced to $\exp(-\beta \delta^+)h$ in the presence of an additional attachment barrier $\delta^+$. Hopping of edge adatoms already at edge sites $(i,1)$ with $1 < i \leq L$ to other edge sites (including the kink site) occurs at rate $h_e$. According to detailed-balance, a step edge adatom at site $(i,1)$ with $2 \leq i \leq L$ hops to terrace site $(i,2)$ on the same terrace with rate $\exp(-\beta \phi^\perp - \beta \delta^+)h$. An adatom at the kink site hops to adjacent step edge sites with rate $\exp(-\beta \phi^\parallel)h_e$, and to the adjacent terrace site $(1,2)$ at rate $\exp(-\beta \phi_b - \beta \delta^+)h$. Consistently, the equilibrium adatom density at the step edge is given by $n_{EQ} = \exp(-\beta \phi_b)n(1,1) = \exp(-\beta \phi_b)$, based on consideration of an equilibrium between terrace and kink adatoms [1, 2, 3].

In addition, we must prescribe the details of interlayer adatom hopping between terraces. We allow for the existence of an additional ES step edge barrier of strength $\delta^-$. This implies that adatoms at sites at an upper step edge $(i,M)$ hop down to adjacent edge or kink sites on the lower terrace at reduced rate $\exp(-\beta \delta^-)h$ relative, which is reduced from that for terrace diffusion. According to detailed-balance, adatoms at the lower step edge sites $(i,1)$ with $1 < i \leq L$ can hop to the adjacent upper terrace site with rate $\exp(-\beta \phi^\perp - \beta \delta^-)h$. The atom at the kink site can hop...
to the adjacent upper terrace site with rate $\exp(-\beta \phi_n - \beta \delta - )h$. Thus, in the special case of an infinite ES barrier ($\delta - = \infty$), there is no transport or “communication” between different terraces.

Appendix C presents a refined version of the discrete 1D deposition-diffusion model of Appendices A and B which better captures the features of our discrete 2D model.

4.2. Discrete 2D deposition-diffusion equations. We assume at a sufficiently low deposition rate that adatom densities are very low and thus adsorption attempts are essentially always successful. Then, the discrete 2D deposition-diffusion equations describing evolution in this model have the steady-state form

$$\frac{d}{dt} n(i,j) = h_{l+1,j}^L n(i+1,j) + h_{i-1,j}^R n(i-1,j) + h_{i,j-1}^U n(i,j-1) + h_{i,j+1}^D n(i,j+1)$$

$$- (h_{i+1,j}^L + h_{i-1,j}^R + h_{i,j+1}^U + h_{i,j-1}^D) n(i,j) + F \approx 0$$

(4) for $1 \leq i \leq L$ and $1 \leq j \leq W$, except for the kink site $(i,j) = (1,1)$, where $n(1,1) = 1$. Here, $h_{i,j}^X$ denotes the rate for hopping from site $(i,j)$ in a direction $X = L$ (left), $R$ (right), $U$ (up), and $D$ (down) in the $(i,j)$-plane. Specific values for any $(i,j)$ follow from the description above. The detailed-balance feature of these rates ensures that the equilibrium solution for $F = 0$ satisfies $n(i,j) = \exp(-\beta \phi_\parallel - \beta \phi_\perp) = \exp(-\beta \phi_n) = n_{EQ}$ for terrace sites $1 < j \leq W$, $n(i,1) = \exp(-\beta \phi_\perp)$ for step edge sites with $1 < i \leq L$, and again $n(1,1) = 1$.

There exists a natural rescaling of the above deposition-diffusion equations setting

$$n^*(i,j) = n(i,j)$$

for terrace sites $2 \leq j \leq W$,

$$n^*(i,1) = \exp(-\beta \phi_\parallel) n(i,1)$$

for step edge sites with $2 \leq i \leq L$, and

$$n^*(1,1) = \exp(-\beta \phi_\perp) n(1,1) = \exp(-\beta \phi_n) n(1,1)$$

for the kink site.

This rescaling ensures that all terms associated with adatom hopping on the right-hand side of the rescaled evolution equations can be written in terms of differences in $n^*$-values for NN pairs of sites. This, in turn, makes transparent the equilibrium solution $n^*(i,j) = n^*(1,1) = n_{EQ}$ for all $(i,j)$ when $F=0$. The rescaling also produces more generic equations in that rescaled densities for all terrace sites satisfy an equation with exactly the same form for zero attachment barriers, $\delta_\pm = 0$, even for sites with $j = 2$ or $j = W$ adjacent to the step edge. This important feature will be exploited below. It is also the case that all edge sites satisfy generic equations (even those adjacent to the kink sites).

Inhomogeneities in the steady-state form of these rescaled equations derive both from deposition terms, and from the coupling to $n^*(1,1)$ of $n^*(i,j)$ with $(i,j)$ neighboring $(1,1)$. It is thus instructive to introduce new variables, $\delta n^*(i,j) = n^*(i,j) - n_{EQ}$ characterizing deviations from equilibrium, so then $\delta n^*(1,1) = 0$. Letting $\delta n^*$ denote a $L \times W$-dimensional vector composed of these quantities, the steady-state form of (3) can be recast in matrix form as

$$A(h_e/h, \phi_\perp) \cdot \delta n^* = (F/h) \varphi(\phi_\perp),$$

(6) where the only inhomogeneity now comes from the deposition terms on the right-hand side. The entries of the nonsymmetric square $(L \times W) \times (L \times W)$ matrix $A$ and vector $e$ can be readily obtained from comparison with (4). The dependence on $h_e/h$ and on $\phi_\perp$ comes from sites at the step edge. In (6), we leave implicit the dependence on attachment barriers $\delta \pm$. There is no dependence on $\phi_\parallel$. The form of (6) immediately
demonstrates that the equilibrium solution for $F = 0$ satisfies $\delta n^* = 0$, consistent with the above observations. Significantly, it also illustrates basic features of non-equilibrium behavior, e.g., the exact proportionality $\delta n^* \propto F$.

The model above was described for a perfect vicinal surface where all terraces have the same width $W$ and kinks are distributed periodically along steps and are aligned in the direction orthogonal to steps. However, the model is readily generalized to treat *more complex vicinal surface geometries*. Our analyses below will often consider bi-periodic systems with alternating broad and narrow terraces, but still with periodically distributed and aligned kinks. In addition, one could consider more complex terrace geometries and arrangements of kinks. In all these cases, there will be a larger rectangular unit cell for which a finite closed set of equations must be analyzed. However, the formulation and structure of the equations is analogous to that above.

4.3. Kinetic coefficients from discrete models. Our focus in this study will be on extracting values for kinetic coefficients, $K_{\pm}$, from analysis of the discrete 2D model for cases where the step permeability term drops out of (2) in the corresponding continuum setting. There are two situations where this scenario applies. The *first* trivial case is for an infinite ES barrier where naturally $P=0$. Then, clearly one has $K_− = 0$, and the task is just to determine $K_+$. The *second* corresponds to cases in a continuum setting where the limiting value of the adatom density is the same approaching any step from either side; i.e., $n_+ = n_−$ in (2) (but these limiting values could differ for different steps). This second situation is realized for a uniform vicinal surface with symmetric attachment barriers, where the adatom density profile is symmetric about the center of the terrace and the same for all terraces. However, to analyze even this case and certainly for more general situations, we must precisely specify a procedure for defining these “limiting values” of adatom densities for the discrete picture.

Given the above remarks, we now specify how values of adatom densities at terrace sites, $n(i, 2 \leq j \leq W) = n^*(i, 2 \leq j \leq W)$, are smoothly extrapolated or “analytically extended” in a precise and unambiguous way to those at the left step $j = 1$ to determine $n^*_+ (i, 1)$, or to those at the right step $j = W + 1$ to determine $n^*_+ (i, W + 1)$. Our basic requirement that the equations for the terrace densities adjacent to the steps (i.e., for $j = 2$ and $j = W$) can be recast into the same generic form as those in the middle of the terraces when incorporating the above extrapolated densities. This formulation is illustrated explicitly in Appendices A and B for a simpler 1D model. An equivalent simpler prescription focuses on the diffusion fluxes, $J_+ (i, 1)$ of adatoms reaching the step $j = 1$ and $J_− (i, W + 1)$ of adatoms reaching the step $j = W + 1$, at the left and right of the terrace along column “i” in the 2D discrete model. We demand that the extrapolated densities $n^*_+ (i, 1)$ and $n^*_+ (i, W + 1)$ satisfy

$$
J_+ (i, 1) = \exp (-\beta \delta_+) h [n^* (i, 2) - n^* (i, 1)] = h [n^* (i, 2) - n^*_+ (i, 1)], \quad \text{and}
$$

$$
J_− (i, W + 1) = \exp (-\beta \delta_-) h [n^* (i, W) - n^* (i, W + 1)] = h [n^* (i, W) - n^*_+ (i, W + 1)].
$$

In section 4.2, we have already noted that for zero attachment barrier on a perfect vicinal surface, the equations for rescaled densities have the generic form for $j = 2$ and $j = W$. This implies that one can make the identification $n^*_+ (i) = n^*_+ (i) = n^* (i, 1) = n^* (i, W + 1)$ consistent with (7) above; i.e., in this case of zero attachment barriers, there is no discontinuity at the step edge in extrapolated values of the rescaled adatom density (i.e., one has $n^*_+ = n^*_+ \Rightarrow n^*_+ = n^*_+ \Rightarrow n^*_+$). Significantly, the corresponding analysis of the equations for rescaled densities for vicinal surface with nonuniform terrace widths
shows that the equality $n^*_i = n^*_j$ is preserved for zero attachment barriers. We exploit this result in our analysis of $K_\pm$ for these cases in section 8.

Next, we provide an explicit prescription for the extraction of kinetic coefficients, $K_\pm$, from our discrete 2D model. To this end, we introduce an average along the step edge direction

$$< B_i >_{\pm} = L^{-1} \sum_{1 \leq i \leq L} B_i,$$

If “a” denotes the lattice constant, then $D = a^2 h$ is the terrace diffusion coefficient, and the deposition flux per unit area in (2) satisfies $F = a^{-2} F$. Motivated by (2), to define $K_\pm$ in the discrete model, we make the replacements

$$a^2(n_+ - n_{eq}) \rightarrow < n^*_+ (i) - n_{eq} >_1 = < \delta n^*_+ (i, 1) >_1$$

$$= < \delta n^*_{\text{edge}} > \text{ (excess edge density),}$$

$$a^2 \nabla n_+ \rightarrow a^{-1} < n^* (i, 2) - n^*_+ (i, 1) >_1 = a^{-1} < \delta n^* (i, 2) - \delta n^*_+ (i, 1) >_1 \text{ (rescaled flux),}$$

recalling that $\delta n^*(i,j) = n^*(i,j) - n_{eq}$. Here, we use that $a^2 n(x)$ corresponds to a density per site with area $a^2$, so, for example, $n_{eq} = a^2 n_{eq}$. Then, to define the kinetic coefficients in the discrete model, we make the replacement

$$(9a) \quad K_+ / D = (\nabla n_+^*) / (n_+ - n_{eq}) \quad \text{in} \quad (2)$$

$$(10a) \quad \rightarrow K_+ / D = a^{-1} < \delta n^* (i, 2) - \delta n^*_+ (i, 1) >_1 / < \delta n^*_+ (i, 1) >_1$$

$$K_\mp / D = (\nabla n_-^*) / (n_- - n_{eq}) \quad \text{in} \quad (2)$$

$$(10b) \quad \rightarrow K_\mp / D = a^{-1} < \delta n^* (i, 2) - \delta n^- (i, 1) >_1 / < \delta n^- (i, 1) >_1,$$

to obtain $K_\pm$ for the step at $j = 1$. Thus, from (6), one has that $K_+ / D = 1 / L_\perp$ depends on $h$ and $h_\perp$ only through the ratio $h_\perp / h$. Perhaps more significantly, $K_\pm$ is independent of $F$. (However, $K_\pm / D$ does depend on $\beta \phi_\perp$ and $\beta \phi_\mp$. A similar analysis applies for $K_-$ and $L_-$ for the step at $j = W + 1$. We emphasize that for zero attachment barriers, one has that $n^*_+ (i, 1) = n^*(i, 1)$ and $n^*_+ (i, W + 1) = n^*(i, W + 1)$ making the above types of formulae explicit.

4.4. Selected properties of steady-states and kinetic coefficients. The kinetic coefficients are determined entirely from the steady-state properties of the solutions of the discrete 2D deposition-diffusion equations, in particular from the ratio of excess density at the steps to the diffusive flux to the step. In a continuum setting, the diffusive flux is constrained by mass conservation; i.e., the amount of material deposited within a region of the terrace must be balanced by the diffusive flux out of that region. This constraint is expressed mathematically by Gauss’ theorem noting that the steady-state form of the continuum deposition-diffusion equations matches that of Poisson’s equation. In the continuum setting, it is also common and instructive to introduce the concept of “capture zones” (CZs) for steps or islands, such that the flux from all points within the CZ flows to that step or island [4]. Then the CZ area times $F$ gives the total diffusive flux to the step or island.

These basic ideas carry over to a discrete setting with some minor modification. The mass conservation constraint described above can be precisely formulated as a discrete version of Gauss’ theorem. One can introduce the concept of CZs although in

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1Consider a region on a terrace including $M$ contiguous sites, such that all hop rates for these and for the adjacent sites are given by $h$. Then, the steady-state form of the discrete deposition-diffusion equations ensures that the total flux, $J_F = h \sum_{B, B'} (n_B - n_{B'}) = h \sum_{B, B'} (n_B - n_{B'})$, out of $M$ equals $M F$. In the expression for $J_F$, we add all contributions between the boundary sites, $B$, in $M$ and the adjacent sites, $B'$, outside of $M$. 

(Continued on the next page)
general the total diffusion flux will not correspond to an integer number of adsorption sites times F. However, effective CZ boundaries can still be selected to reflect the total diffusion flux. As a simple example, mass conservation for infinite ES barrier and $\delta_e = 0$ yields the relation

$$J_+ = < J_+ (i, 1) > = h < n^*(i, 2) - n^*(i, 1) >_1 = h < \delta n^*(i, 2) - \delta n^*(i, 1) >_1 = F(W - 1)$$

for the total flux reaching the ascending step. As discussed in section 2.2, the step velocity is determined by the total flux of atoms reaching the step. In addition to the diffusive components, this always includes a component, $J_{dd}$, due to direct deposition at the step edge. For a perfect vicinal surface with terraces of width W, mass conservation implies that $J_+ + J_- + J_{dd} = FW$.

Now, we turn to analysis of the dependence of the kinetic coefficients on specific model parameters. First, we remark that the limiting case $h_e \to \infty$ is of special interest since it produces *equilibration of the step edge density*, $n^*(i, 1) \to n_{EQ}$. In fact, the discrete 2D deposition-diffusion equations reduce to the 1D equations of Appendices A and B by virtue of translational invariance along the step direction. Then, simpler “traditional” results for kinetic coefficients immediately follow. In particular, $K_+ = \infty$ with attachment barrier $\delta_e = 0$, and $K_- = \infty$ with zero ES barrier $\delta_e = 0$. Thus, an appealing feature of our model is the ability to tune the degree of equilibration (or lack thereof) by adjusting $h_e$ relative to $h$.

For finite step edge diffusion rates $h_e < \infty$, we will obtain finite values for the effective $K_{\pm}$ even in the absence of attachment barriers. This is because incorporation at steps is inhibited by a “small” kink density, which results in a strictly positive excess edge density $< \delta n_{edge}^* >$. From this perspective, it is expected that $K_{\pm}$ should vanish with increasing kink separation $L \to \infty$. To elucidate this regime and the associated behavior of $K_{\pm}$, it is natural to introduce a *semidiscrete version* of the fully discrete model described in section 4.1. Here, the discrete density, $n(i, j)$, in the step direction $i$ for large $L$ is replaced by a semicontinuous quantity, $n(x, j)$, where the continuous position $x$ corresponds to $ia$. One then analyzes a finite coupled set of continuous deposition-diffusion equations for the $n(x, j)$ for $0 < x < aL$ and $1 \leq j \leq W$, where these densities extend periodically to other $x$. See Appendix D. The resulting analysis indicates that

$$K_{\pm}(L) \approx A/L^2 \text{ as } L \to \infty.$$ 

Furthermore, behavior for a broad range of $L$ should be well described by $K_{\pm}(L) \approx A/(L^2 + BL + C)$. Since $K_{\pm}$ are given by the ratio of the attachment flux and the excess step density, the result (12) is understood from the feature that the attachment flux is independent of $L$ [cf. (11)], and the excess step density naturally scales like $L^2$. As noted in section 2.2, considerations of kink attachment-limited step flow in liquid-phase crystal growth naturally led to kinetic coefficients which decrease with increasing kink separation. The functional form of $K_{\pm}$ versus $L$ is different here since we are considering diffusion-limited kink attachment.

Results for $K_{\pm}$ with finite $h_e < \infty$ will also depend on the width, $W$, of the terrace on the vicinal surface. Since coarse-grained models are usually applied to situations where the typical kink separation is well below other characteristic lengths (e.g., typical terrace widths), it is natural to examine the behavior of $K_{\pm}$ in the limit of broad terraces, $W \to \infty$. For an infinite ES barrier with $\delta_e = 0$, using that $h < \delta n^*(i, 2) - \delta n^*(i, 1) >_1 = F(W - 1)$ from (11). Then, provided that the excess
adatom density at steps is roughly proportional to the terrace width \( <\delta n^*_{\text{edge}} > \propto W \), it follows that

\begin{equation}
K_\pm(W) \approx K_\pm(\infty) \frac{(W - 1)}{W}.
\end{equation}

As a sample numerical test of this W-dependence of \( <\delta n^*_{\text{edge}} > \) for \( L=50, h = h_e \), and \( \beta \phi_\perp = 1 \), we find that \( <\delta n^*_{\text{edge}} > \approx 0.00305W + 4.2 \times 10^{-8} \) for W ranging from 50 to 500.

5. Infinite ES barrier \( \delta_+ = \infty \) and zero attachment barrier \( \delta_- = 0 \).

This case of an infinite ES barrier, \( \delta_- = 0 \), has the simplifying feature that atoms cannot attach to a step from the upper terrace (i.e., \( K_- = 0 \)), and thus that steps are impermeable (i.e., \( P = 0 \)). Then (2) reduces to the zero-flux BC \( \nabla n|_{-} = 0 \) at descending steps. In such systems, behavior on each terrace is completely independent. We consider in section 5 only the case of zero step attachment barrier to the step, \( \delta_+ = 0 \). Our focus is on the determination of the kinetic coefficient, \( K_+ \), describing attachment to the ascending step. Here, the step velocity is just determined by the width of the associated lower terrace (and by the deposition flux) which constitutes the CZ for the step.

Typical behavior of the rescaled densities \( \delta n^*(i, j) \) is shown in Figure 4 for \( h = h_e \) and \( h/F = 10^4 \) with \( L = 20, W = 20 \), and \( \beta \phi_\perp = 1 \). Note the increase in the step edge densities \( \delta n^*(i, 1) \) between the kink sites above \( n_{\text{eq}} \). The traditional view for this case would be that \( K_+ = \infty \) forcing the classic BCF BC that \( n_+ = n_{\text{eq}} \). However, as already noted in section 4, we find finite values of \( K_+ \) due to inhibited incorporation at kinks.

![Fig. 4. Three-dimensional (3D) plot of scaled excess adatom density, \( \delta n^*(i, j) \), for infinite ES barrier, \( h_e = h \), and \( h/F = 10^4 \) with \( L = 20, W = 20 \), and \( \beta \phi_\perp = 1 \). The foreground of the plot shows the kink sites at \( i = 1 \) and \( i = 21 \), where the adatom density is lowest, and also the variation of adatom density along the step edge peaking midway between the kink sites.](image-url)

Next, we consider the dependence of \( K_+ \) on terrace geometry. In Figure 5(a), we show results for \( K_+ \) versus kink separation \( L \) for \( h_e/h = 1 \) with fixed \( W = 100 \) and \( \beta \phi_\perp = 1 \). It is clear that \( K_+ \to 0 \) as \( L \to \infty \), and for larger \( L \) this decrease is
described by (12). Note that for \( L = 1 \) (an entire step edge composed of kinks), the model reduces to a 1D model with a standard BCF Dirichlet BC so that \( K_+ = \infty \).

Next, in Figure 5(b), we show results for \( K_+ \) versus terrace width \( W \) for \( h_e/h = 1 \) with fixed \( L = 40 \) and \( \beta \phi_{\perp} = 1 \). It is clear that \( K_+ \) converges to a finite value as \( W \to \infty \), and that the functional form is described well by (13), where \( aK_+(\infty)/D = 0.0455 \).

See Table 1 for a list of values of \( K_+(\infty) \) for various \( L \).

![Fig. 5. Behavior of \( K = K_+ \) for an infinite ES barrier and \( \delta_+ = 0 \) for \( h_e/h = 1 \) and \( \beta \phi_{\perp} = 1 \): (a) \( K_+ \) versus \( L \) with fixed \( W = 100 \); (b) \( K_+ \) versus \( W \) with fixed \( L = 40 \).](image)

### Table 1

<table>
<thead>
<tr>
<th>Kink spacing, ( L )</th>
<th>( aK_+(\infty)/D ) for ( \delta_+ = \infty, \delta_+ = 0 )</th>
<th>( aK_+(\infty)/D ) for ( \delta_+ = 0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.133647</td>
<td>0.088766</td>
</tr>
<tr>
<td>40</td>
<td>0.045592</td>
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<tr>
<td>60</td>
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</tr>
<tr>
<td>150</td>
<td>0.007158</td>
<td>0.005702</td>
</tr>
<tr>
<td>200</td>
<td>0.004905</td>
<td>0.003971</td>
</tr>
</tbody>
</table>

Now, we turn to consideration of the dependence of \( K_+ \) on model dynamics and energetics. We have already noted that \( K_+ \) depends only on the ratio \( h_e/h \) rather than on \( h \) and \( h_e \) separately. Behavior is shown in Figure 6(a) for \( L = 30, W = 100 \), and \( \beta \phi_{\perp} = 1 \). Apart from some nonlinear variation for small \( h_e/h < 1 \), behavior is essentially linear \( K_+ \sim c \cdot h_e/h \). This form recovers the classic result \( K_+ \to \infty \) as \( h_e \to \infty \) in the absence of an attachment barrier. This limiting behavior is due to complete equilibration of the adatom density at the step edge. The asymptotic linear dependence derives from the feature that the flux \( J_+ \) converges to a finite value for \( h_e = \infty \), and the deviation of step edge densities from equilibrium scales like \( <\delta n_{edge}^* > \sim h_e/h \).

Finally, we consider the dependence of \( K_+ \) on \( \beta \phi_{\perp} \). Intuitively, stronger bonding to the step edge should facilitate capture of diffusing adatoms at kinks. Thus, \( K_+ \) should increase with increasing \( \beta \phi_{\perp} \). For \( \beta \phi_{\perp} = 0 \), where capture is least efficient, \( K_+ \) should still retain a finite nonzero value. Numerical results are presented in Figure 6(b) for \( L = W = 50 \) and \( h = h_e \) (where \( aK_+/D = 0.02097 \) for \( \beta \phi_{\perp} = 0 \) and \( aK_+/D = 0.03216 \) for \( \beta \phi_{\perp} = 1 \)) confirming this behavior. To further elucidate this behavior, we note that as \( \beta \phi_{\perp} \to \infty \), an exact analysis is possible for the fundamental equations (4).
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Fig. 6. Behavior of $K = K_+$ for an infinite ES barrier and $\delta_\pm = 0$: (a) $K_+$ versus $h_e/h$ for $L = 30$, $W = 100$, and $\beta_\phi \perp = 1$; (b) $K_+$ versus $\beta_\phi \perp$ for $h_e/h = 1$ and $L = W = 50$.

or (5). In this regime, the equations for the rescaled adatom density on the terraces all have the generic form. However, equations for the rescaled adatom densities along the step edge decouple from the terrace densities reducing to a simple 1D discrete diffusion equation (provided that $h_e > 0$) with a vanishing deposition source. Thus, the steady-state solution for these edge densities approaches the equilibrium value. Correspondingly, since $<\delta n^*_\text{edge}> \to 0$, one has that $K_+ \to \infty$.

6. Zero attachment barriers $\delta_\pm = 0$: Perfect vicinal surfaces. We consider here the case of a perfect vicinal surface with terraces of width $W$ and no attachment or ES barriers, $\delta_\pm = 0$, where by symmetry one has that $n^*_+ = n^*_-$ and that $K_+ = K_-$. In this case, since all steps are equivalent, it is clear that the step velocities are the same for all steps and that these are just determined by the single terrace width, $W$ (and the deposition flux). By symmetry together with application of the discrete Gauss’ theorem, the attachment fluxes from both sides of each step are equal, and adopt a value $J_\pm = \frac{1}{2} F(W-1)$. In the case, the CZ for each step extends symmetrically to the midpoint of the terrace on either side. Since the total flux to each step is the same as for the case of infinite ES barrier, one might expect similar excess step densities, $<\delta n^*_\text{edge}>$. In fact, we find this density for $\delta_\pm = 0$ is larger than that for the case of infinite ES barrier in section 5, which implies that the $K$-value is smaller. See Table 1.

First, we consider the dependence of $K_\pm$ on terrace geometry. We find that that $K_\pm \to 0$ as kink separation $L \to \infty$. For larger $L$, the functional form of this decrease is described by (12) as follows from analysis of an appropriate semidiscrete version of the model. For $L = 1$, the 2D model reduces to a 1D model with a standard BCF BC so that $K_\pm = \infty$. As an aside, the value of $K_\pm$ for kink separation $L$ with $\delta_\pm = 0$ is the same as the value of $K_\pm$ for infinite ES barrier ($\delta_\pm = \infty$) with $\delta_\pm = 0$ for kink separation $1.25L$ (with the same $W$ and $\beta_\phi \perp$). In addition, we have examined the convergence of $K_\pm$ to a finite value as $W \to \infty$, and the functional form is described well by (13) given in section 4.4 just as for the case of infinite ES barrier. See Table 1 for a list of values of $K_\pm(\infty)$ for various $L$.

Next, we turn to consideration of the dependence of $K_\pm$ on model dynamics and energetics. Apart from some nonlinear variation for $h_e/h < 1$, one finds an essentially linear variation $K_\pm \sim c \cdot h_e/h$. This follows since $J_\pm$ converge to a finite value for $h_e = \infty$, and one expects that $<\delta n^*_\text{edge}> \sim h/h_e$ just as for the case on infinite ES barrier. Finally, we consider the dependence of $K_\pm$ on $\beta_\phi \perp$. $K_\pm$ increases with increasing $\beta_\phi \perp$ from a nonzero value for $\beta_\phi \perp = 0$, where capture is least efficient, and $K_\pm \to \infty$ as $\beta_\phi \perp \to \infty$, i.e., the same behavior for the same reasons as with...
an infinite ES barrier. For \( L = W = 50 \) and \( h = h_e \), one has \( aK_+ / D = 0.01666 \) for \( \beta \phi_{\perp} = 0 \) and \( aK_+ / D = 0.02357 \) for \( \beta \phi_{\perp} = 1 \).

7. Zero attachment barriers \( \delta_{\pm} = 0 \): Imperfect vicinal surfaces. Here, we consider the case of imperfect vicinal surfaces with a distribution of terrace widths. For simplicity, we assume the same density (or separation) of periodically distributed kinks on all steps. Again, kinks on different steps are aligned in the direction orthogonal to the steps. A key feature is that for any distribution of terrace widths in the absence of attachment and ES barriers, the limiting value of the adatom density is the same approaching each step from either side; i.e., \( n_+ = n_- \) in (2), or \( n^*_+ = n^*_- \) in the discrete model. Thus, the step permeability term still drops out of (2), and we can determine the (generally different) values of \( K_+ \) and \( K_- \) for each step based on the algorithm described at the end of section 4.

7.1. Biperiodic vicinal surfaces. We consider here the simplest “imperfect case” of a biperiodic vicinal surface with alternating narrower and broader terraces of widths \( W_a \) and \( W_b \). In this case, by reflection symmetry, there is a single excess adatom density \( <\delta n^*_{\text{edge}}> \) at both types of steps. Also, the adatom density profile is symmetric about the middle of each type of terrace. A typical adatom density profile averaged along the steps is shown in Figure 7 for the case of kink spacing \( L = 50 \), terrace widths \( W_a = 50 \) and \( W_b = 100 \), \( h_a = h_b \), and \( \beta \phi_{\perp} = 1 \). It is clear that the CZ for each step extends to the midpoint of the terraces on either side. It is also clear that the velocities of all steps are identical.

In further analysis, we just focus on behavior in the regime of broad terraces. Let \( K_{\pm}^a \) denote the kinetic coefficients for a biperiodic vicinal surface associated with terraces of widths \( W_a \) and \( W_b \). By symmetry, one has that \( K_{+}^a = K_{-}^a \) and \( K_{+}^b = K_{-}^b \) since the flux to steps on either side of the same terrace is identical, and since there is a single excess adatom density at steps. Then,

![Figure 7](https://example.com/figure7.png)

**Fig. 7.** Scaled excess adatom density profile \( <\delta n^*_{\text{edge}}> \) across the terraces (averaged along steps) for a biperiodic system with terrace widths \( W_a = 50 \) and \( W_b = 100 \) and zero attachment barriers \( \delta_{\pm} = 0 \). Other parameters are \( h_a = h_b / F = 10^3 \), \( L = 50 \), and \( \beta \phi_{\perp} = 1 \). Note the unique excess adatom density at step edges, but the distinct attachment fluxes from different sides of the steps.
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it follows that

\[ K_b^+ / K_a^+ \approx W_b / W_a. \]  

In addition, from numerical data, we find that

\[ K_a^+ + K_b^+ \approx 2K_\pm(\infty), \]  

where \( K_\pm(\infty) \) denotes the value of the kinetic coefficients for a perfect vicinal surface in the limit of broad terraces, and with the same kink density as the biperiodic case. As an example, for kink separation \( L = 50 \) with \( h_c = h \) and \( \beta\theta_\perp = 1 \), where \( 2nK_\pm(\infty)/D = 0.048158 \), we find that for very broad terraces one has \( aK_\pm^+ / D = 0.032105 \) and \( aK_\pm^- / D = 0.016053 \) for \( W_b/W_a = 2 \).

The relation (15) can be understood in terms of the behavior of the single excess adatom step density, \( <\delta n_{\text{edge}}^+>_B \), in the biperiodic system. Let \( <\delta n_{\text{edge}}^+>_a \propto W_a \) denote the excess density for a perfect vicinal surface with finite terrace width \( W_a \), etc. Provided that the excess adatom density is just determined by the average 2D kink density in the system, then it immediately follows that

\[ \frac{1}{2} (W_a + W_b) / <\delta n_{\text{edge}}^+>_B \approx W_a / <\delta n_{\text{edge}}^+>_a \approx W_b / <\delta n_{\text{edge}}^+>_b, \]  

which is equivalent to the sum rule (15). An equivalent perspective comes from the observation that (16) implies that the excess adatom step density \( <\delta n_{\text{edge}}^+>_B \) in the biperiodic systems equals that for a perfect vicinal surface with terrace width equal to the average of the terraces in the biperiodic system.

7.2. Triperiodic and other vicinal surfaces. Consider triperiodic vicinal surfaces with cyclically alternating terraces of width \( W_a, W_b, \) and \( W_c \), but the same kink separation \( L \) on all steps. This case is more representative of the general situation. Here, there are three types of steps: \( S_{ab} \) separating terraces of width \( W_a \) and \( W_b \), and similarly \( S_{bc} \) and \( S_{ac} \). For each step, there are in general two distinct kinetic coefficients \( K_{ab}^\pm \) for \( S_{ab} \), etc. No longer is it possible to simply determine diffusive fluxes to steps since the boundaries of the CZs for each step do not necessarily correspond to the middle of the terraces on either side. Also, in general, each step has a different excess adatom density. However, from numerical analysis for broad terraces, we find analogous to (15) that

\[ K_{ab}^+ + K_{ab}^- + K_{bc}^+ + K_{bc}^- + K_{ac}^+ + K_{ac}^- \approx 6K_\pm(\infty), \]  

where \( K_\pm(\infty) \) denotes the value of the kinetic coefficients for a perfect vicinal surface in the limit of broad terraces, and with the same kink density as the triperiodic case. For example, in the case where \( W_a = 22m, W_b = 30m, W_c = 37m \), and \( L = 50 \), we show the adatom density profile in Figure 8 and give all six K-values in Table 2 for the case \( m = 5 \). More generally, we find that the values of the above 6 \( aK/D \)-values sum to 0.136766, 0.143657, 0.143983, and 0.144424 for \( m = 1, 5, 10, \) and 100, respectively, which should be compared with 6 \( aK_\pm(\infty)/D = 0.144473 \).

In contrast to all the previous examples, in the case of the triperiodic vicinal surface, the step velocities differ and are nontrivial. According to the general strategy laid out in section 2, knowledge of the six K-values (e.g., from Table 2 for \( m = 5 \)) together with the result (3) allows determination of the diffusive fluxes to each step. Then, adding the simple constant contribution from direct deposition at each step.
Fig. 8. Scaled excess adatom density profile $<\delta n^*>$ across the terraces (averaged along steps) for triperiodic case with terrace widths $W_a = 22m$, $W_b = 30m$, and $W_c = 37m$ for $m = 5$, and zero attachment barriers $\delta_\pm = 0$. Excess adatom densities at the steps are $<\delta n^*_a > \approx 0.0305$, $<\delta n^*_b > \approx 0.0282$, $<\delta n^*_c > \approx 0.0336$. Other parameters are $h = h/F = 10^5$, $L = 50$, and $\beta \phi_\perp = 1$. Note the distinct excess adatom densities at different steps.

Table 2

<table>
<thead>
<tr>
<th>$aK_a^+/D$</th>
<th>$aK_b^+/D$</th>
<th>$aK_c^+/D$</th>
<th>$aK_a^-/D$</th>
<th>$aK_b^-/D$</th>
<th>$aK_c^-/D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.020269</td>
<td>0.017307</td>
<td>0.021182</td>
<td>0.027904</td>
<td>0.030848</td>
<td>0.026965</td>
</tr>
</tbody>
</table>

allows determination of the step velocities. It is appropriate to compare the results of our analysis with those from a classical BCF treatment where the adatom densities are symmetric about the center of each terrace. Thus, the diffusive flux to the steps on the left and right side of each terrace is equal (as for any case with equal K-values for the left and right steps). Thus, deviations from classical BCF behavior are due to a difference between K-values for the steps at the left and right ends of the different terraces (cf. Table 2). The fact that the attachment lengths associated with the K-values are of the order of the terrace widths means that these deviations are significant.

To interpret the sum rule (17) in terms of the excess adatom step densities, let $<\delta n^*_{\text{edge}}>_a$ denote this density for a perfect vicinal surface with broad terraces of width $W_a$, etc. For the triperiodic vicinal surface, let $<\delta n^*_{\text{edge}}>_ab$ denote the excess adatom density at step $S_{ab}$, and let $W_{ab}^\pm$ denote the width of the CZ for this step on the lower (+) and upper (−) terrace. Thus, $W_{ab} = W_{ab}^+ + W_{ab}^−$ denotes the full width of the CZ on both sides of the step. These quantities are defined analogously for other steps. Then, it follows that $W_{ab} + W_{bc} + W_{ac} \approx W_a + W_b + W_c$. See Figure 8. Also since $K_{ab}^+ \propto W_{ab}^+/<\delta n^*_{\text{edge}}>_a$ and $K_{bc}^+ \propto W_{ab}/<\delta n^*_{\text{edge}}>_b$, etc., (17) is instructively recast as

$$W_{ab}/<\delta n^*_{\text{edge}}>_a + W_{bc}/<\delta n^*_{\text{edge}}>_b + W_{ac}/<\delta n^*_{\text{edge}}>_c$$

$$= W_a/<\delta n^*_{\text{edge}}>_a + W_b/<\delta n^*_{\text{edge}}>_b + W_c/<\delta n^*_{\text{edge}}>_c,$$

(18)
where all three terms on the right-hand side have the same value. In special cases for triperiodic systems, e.g., where two of the terraces have equal width, then (18) can be reduced further.

For another perspective leading to a more complete analysis, we note that the K’s for the triperiodic system correspond to those from various biperiodic systems for suitable choices of terrace widths (and the same kink separation $L$). For example, $K_{ab}^{ab}$ above corresponds to K’s in a biperiodic system with terraces of width $2W_{ab}^+$ and $2W_{ab}^-$, where $K_{ab}^{ab}$ ($K_{ab}^+$) corresponds to $K_{ab}$ for the terrace of width $2W_{ab}^+$ ($2W_{ab}^-$). Then $\langle \delta n_{edge}^* \rangle_{ab}$ corresponds to the unique excess adatom step density in this biperiodic system. See Figure 9. Thus, $W_{ab}/\langle \delta n_{edge}^* \rangle_{ab} = W/\langle \delta n_{edge}^* \rangle_{bc}$ for any perfect vicinal surface with terraces of width $W$ and excess adatom step density $\langle \delta n_{edge}^* \rangle$. Extending this analysis for other steps recovers (18).

Fig. 9. Schematic comparing: (a) scaled excess adatom density profile across the terraces (averaged along steps) for a triperiodic system; and (b) the profile in one of the “corresponding” biperiodic systems. Also indicated are the widths of terraces and of various CZs, as well as the boundaries of those CZs ($\partial$CZ).

In more general cases of vicinal surface with higher-order periodicity, one finds a natural generalization of (15) or (17). Broader terraces with smaller neighbors tend to have larger K-values, and the opposite is true for smaller terraces with broader neighbors. The demonstration of these general K-sum rules follows from extending the analysis in the previous paragraph.
8. Other cases without a permeability contribution. In addition to the cases discussed in sections 5, 6, and 7, there are other situations (some are discussed here) where the limiting value of the adatom density is the same approaching each step from either side; i.e., \( n^+ = n^- \) in (2), or \( n_1^+ = n_1^- \) in discrete models. Thus, again the step permeability term still drops out of (2), and \( K^\pm \) can be determined from the algorithm in section 4.

8.1. Finite attachment barriers. For the case of an infinite ES barrier where \( P = 0 \) and behavior on each terrace is isolated from or independent of that on other terraces, we consider the effect of including a nonzero step attachment barrier \( \delta_+ > 0 \) to the ascending step. Intuitively, one expects that the step edge density “behind the attachment barrier” should become more equilibrated and spatially uniform with increasing \( \delta_+ \). As a result, behavior should reduce to that of the 1D model with an attachment barrier in Appendix A. Consequently, \( K_+ = D/L_+ \) should asymptote to the 1D result where \( L_+ \sim \exp(\beta \delta_+) \), as \( \delta_+ \to \infty \). This behavior is indeed realized and shown in Figure 10(a) for \( h_e/h = 1, L = 50, W = 50, \) and \( \beta \phi_\perp = 1 \), and \( D/(aK_+) \approx \exp(\beta \delta_+) + 77.2 \) for large \( \delta_+ \).

For a perfect vicinal surface with terraces of width \( W \), we consider the case of symmetric nonzero step attachment barriers \( \delta = \delta_+ = \delta_- > 0 \). Here, by symmetry, the limiting value of the adatom density is the same approaching the step from either side (i.e., \( n_1^+ = n_1^- \)), and one also has that \( K_+ = K_- \). Again, since the step edge density “behind the attachment barrier” should become more equilibrated with increasing \( \delta_\pm \), behavior should reduce to that of the 1D model, so \( K_\pm = D/L_\pm \) should asymptote to the 1D result \( L_\pm \sim \exp(\beta \delta) \). This behavior is shown in Figure 10(b) for \( h_e/h = 1, L = 50, W = 50, \) and \( \beta \phi_\perp = 1 \), and \( D/(aK_\pm) \approx \exp(\beta \delta) + 155.3 \) for large \( \delta \). One might anticipate that we could extend consideration of the case of symmetric nonzero step attachment barriers to imperfect vicinal surfaces and still retain the equality \( n_1^+ = n_1^- \). However, numerical data for a biperiodic vicinal surface with \( W_a \neq W_b \) demonstrates that this is not the case—the adatom density for the broader terraces extrapolating to a higher value at the step edge. In fact, this behavior is consistent with the relations (7) determining extrapolated densities.

8.2. Varying kink separations on AB-vicinal surfaces. Finally, in contrast to all cases considered above in this and previous sections, we consider a situation where the kink separation differs on different steps. Motivated by the anisotropic SOS

![Fig. 10. Variation of K-value with finite attachment barrier for h_e/h = 1, L = 50, W = 50, and \( \beta \phi_\perp = 1 \): (a) \( D/(aK_+) \) versus \( \beta \delta \) with \( \delta = \delta_+ \) for an infinite ES barrier; (b) \( D/(aK_\pm) \) versus \( \beta \delta \) for symmetric attachment barrier \( \delta_\pm = \delta \). The solid curves show the function \( \exp(\beta \delta) \) versus \( \beta \delta \).](image-url)
model described in section 3 which provides a simple model for an AB-vicinal surface, we specifically analyze the case where the kink separation alternates between \( L \) and \( nL \) (with \( n > 1 \)) on a vicinal surface where all terraces have width \( W \). We choose \( L = 40 \), \( n = 2 \), and \( W = 15 \). Different kink densities on different steps correspond to different attractive interactions between adatoms in the direction of the step edge. Using the terminology of the anisotropic SOS model, we choose \( \beta \phi_s = 5.06 \) and \( \beta \phi_w = 4.36 \) to be consistent with our choice of kink separations [30]. Thus, in our discrete 2D deposition–diffusion equation modeling, we choose different values of \( \beta \phi_\perp \) for the two types of steps alternating between \( \beta \phi_s \) for B-type steps with \( L = 40 \), and \( \beta \phi_w \) for A-type steps with \( L = 80 \). A schematic of the steady-state adatom density for this choice of parameters is shown in Figure 11.

Quantitative analysis of the above system yields \( aK/D \)-values of 0.589 for the B-type step with higher kink density (\( L = 40 \)), and 0.0817 for the A-type step with lower kink density (\( L = 80 \)). Then, application of (3) allows determination of the diffusive flux to each step. We find the ratio of diffusive fluxes to A-type and B-type steps is 0.47 (the former being smaller). Accounting for direct deposition at steps on terraces of width \( W = 15 \), one obtains a slightly modified ratio of total fluxes to A-type and B-type steps of 0.49. Thus, if \( V_A \) (\( V_B \)) denotes the velocity of A-type (B-type) steps for the configuration of Figure 11, it follows that \( V_A/V_B = 0.49 \). As might be expected given the higher \( K \)-value that the B-type step has the higher velocity, consistent with simulation results of section 3. An independent way to assess the

**Fig. 11.** Scaled excess adatom density \( \delta n^*(i,j) \) for system with alternating kink density on adjacent steps. We choose kink separations of \( L = 40 \) and \( L = 80 \), a terrace width of \( W = 15 \), and set \( h_e = h \), \( h/F = 10^9 \), and \( \beta \phi_\perp = 1 \). The plot also shows location of the kinks and the nonlinear CZ boundaries (\( \partial CZ \)).
differing step velocities is provided by Figure 11 where we also show the boundaries ($\partial$CZ) of the CZs for both steps. Clearly, the B-type step with higher kink density has a significantly larger CZ (quantified below), consistent with the larger velocity. In summary, the different $K$-values for different steps induce different velocities even starting with a perfect “equilibrium” AB-vicinal surface with uniform terrace widths.

One might hope that this system could be analyzed in terms of simpler systems with a single kink separation of $L$ and of $nL$ and the appropriate choice of $\beta \phi_\perp$ (cf. our analysis of triperiodic systems in terms of biperiodic systems). However, in contrast to such analyses above, such an exact analysis is not possible since, e.g., the CZ boundary between the two steps is not a straight line. See Figure 11. Despite this feature, one can still define an average width, $W_\neq = 20.3$ ($W_\leq = 9.7$), of the CZ for the B-type (A-type) step, where $W_\neq + W_\leq = W$. In fact, we note that $W_\leq/W_\neq = 0.48$ quite consistent with the above estimate of the ratio of step velocities $V_A/V_B$. Then, to a first approximation, the step edge with kink separation $L$ will have the same $<\delta n_{\text{edge}}>$ as for a perfect vicinal terrace width $2W_\neq$ with kink separation $L$ and the appropriate value of $\beta \phi_\perp$ and the other parameters (and analogously for the step with fewer kinks). Consequently, $K_\pm$ for the B-type (A-type) step should roughly equal the value of these quantities for a perfect vicinal surface with kink separation of $L$ ($nL$) and suitable choices of other parameters. The CZ boundaries in Figure 11 are quite bent, limiting the accuracy of the above approximation, but we have checked its validity in other cases with straighter boundaries.

9. Summary. We have implemented a new strategy to obtain insight into the appropriate kinetic coefficients, $K_\pm$, for BCF type BCs for step flow under nonequilibrium conditions. Our approach prescribes as input the geometry of the vicinal surface including the distribution of kinks along step edges. Then, we solve discrete 2D deposition-diffusion equations for this geometry to determine the adatom density distribution, and thus fluxes of attachment at (kinks along) step edges. We obtain explicit values for the $K_\pm$ mostly for cases where there is no barrier to attachment to steps and where the step permeability is not relevant. Specifically, we characterize the dependence of the $K_\pm$ on the kink density and terrace width, and also obtain a sum rules for these coefficients for imperfect vicinal surfaces with different terrace widths. The systems considered would traditionally be described by the classical BCF picture which equates the adatom density to its equilibrium value at the step edge (corresponding to $K = \infty$). However, this classical treatment fails to capture such phenomena as nonequilibrium step pairing observed in an anisotropic SOS model of an AB-vicinal surface with alternating types of steps [18]. In contrast, our approach is successful.

Our new approach is somewhat complementary to other recent mean-field rate equation modeling based on the terrace-step-kink picture [12, 13, 14, 15, 16, 17]. As noted previously, this approach specifies diffusion fluxes or adatom densities at steps as input and determines the dynamic steady-state step structure (in contrast to our specification of step structure and solution of the deposition-diffusion equations). However, both our analysis and that of MC [17] assess kinetic coefficients. We obtain precise numerical values and assess dependences on various geometric parameters for arbitrary energetic and diffusion parameters. MC perform a perturbation analysis to obtained general expressions in the regime of small Peclet number (large edge diffusion). Thus, direct comparison is difficult. However, there is consistency, e.g., between our increase in $K$-values with increasing kink density and MC’s increase with increasing step misalignment.
One perspective on the shortcomings of the classical BCF picture, motivating and highlighted in our work, is that it is geared towards situations with high kink densities and efficient equilibration of the adatom density at step edges. However, for typical kink densities along steps, there is always some inhibition to equilibration (less facile equilibration corresponding to smaller kinetic coefficients). To assess the degree of equilibration, it is instructive to introduce attachment lengths \( L_{\pm} = D/K_{\pm} \) (less facile equilibration corresponding to larger attachment lengths). The classical BCF picture does apply in the regime where typical terrace widths far exceed attachment lengths (corresponding to a quantitative characterization of “high kink density”). However, in the case of step pairing described above, this condition is not met. More generally, it is known that traditional continuum near-equilibrium treatments may fail when the relevant characteristic length in the system becomes comparable to natural length scales determined by the microscopic parameters of the model. For example, for diffusion and shape-relaxation of 2D islands on surfaces mediated by edge diffusion, this failure occurs when the linear size of the island becomes comparable to the equilibrium kink separation or to another characteristic length associated with inhibited edge diffusion [35, 36].

In our analysis above, with one exception, we have restricted our attention to cases where the limiting value of the adatom density is the same approaching the step from either side; i.e., \( n_+ = n_- \) in (2), or \( n^*_+ = n^*_− \) in the discrete model. This means that the permeability term drops out of the traditional BCF BC allowing us to determine the kinetic coefficients \( K_{\pm} \) in an unambiguous fashion. It should be emphasized, however, that except in the case of infinite ES barrier discussed in section 5, the steps in our 2D discrete deposition-diffusion equation model should be regarded as permeable. Adatom diffusion across steps is possible without incorporation at kinks. In fact, one would expect permeability to increase with decreasing bond strength \( \phi_{\perp} \) and decreasing step edge hop rate \( h_e \). In a more general context, interest in and the importance of step permeability arose in near-equilibrium situations were there were spatial nonuniformities in chemical potential of adatoms causing flow across permeable steps [10, 19]. In future work, we will explore various strategies to provide insight into step permeability in our model.

Appendix A: Discrete 1D deposition-diffusion model for stepped surfaces. In this “standard” discrete 1D model, the stepped surface is described by a 1D array of sites labeled \( j = \ldots, −2, −1, 0, 1, 2, \ldots \) with positions \( x_j = ja \), where “a” denotes the surface lattice constant. These sites correspond to rows of sites parallel to the step edge in the 2D model. We focus on the region surrounding a step edge or “step site” at \( j = 0 \), where sites \( j = −1, −2, \ldots \) are on the adjacent upper terrace, and \( j = 1, 2, \ldots \) are on the lower terrace. As in our 2D modeling, we also assume that attachment and detachment from the step edge do not alter the step location from \( j = 0 \). Thus, we adopt a quasi-static type approximation where step motion is regarded as slow compared to relaxation of the adatom diffusion field. However, one key simplification in this model relative to the 2D case is that we assume that the adatom density right at the step edge is equilibrated. We can allow direct deposition at the step site, but this does not affect analysis of the steady-state adatom density, rather just adding a simple contribution to the step velocity. See Figure 12 for a schematic. Notation is selected by analogy with our 2D model. We let \( n(j) \) denote the adatom density at site \( j \), and set \( n(0) = 1 \) at the step site. \( F \) denotes the deposition flux per site; \( h \) denotes the rate of hopping between adjacent terrace sites; \( h_{\pm} = \exp(−\beta\delta_{\pm})h \) denote the possibly modified hop rates from the adjacent terrace site \( j = \pm 1 \) to the step site.
Fig. 12. Schematic of adatom density in the standard 1D discrete deposition-diffusion model in the vicinity of a step edge. Also shown are, the adatom hop rates, total diffusion fluxes reaching the step edge, \( J_{\pm} \), the flux across the step due to permeability, \( J_p \), and the flux to the step due to “direct deposition”, \( J_{dd} \). The latter does not affect the adatom density analysis.

\( n = 0 \) due to attachment barriers \( \delta_{\pm} \); and \( h_p \) denotes the rate of direct hopping between sites \( j = +1 \) and \( -1 \) (reflecting a direct channel for step permeability). Corresponding diffusion coefficients are denoted by \( D = a^2 h \), \( D_{\pm} = a^2 h_{\pm} \), and \( D_p = a^2 h_p \). Finally, we let \( \phi_b \) denote the strength of the bonding of adatoms at step edges (corresponding to bonding at kink sites in a 2D model). As a result, \( n_{EQ} = \exp(-\beta \phi_b) n(0) = \exp(-\beta \phi_b) \) represents the equilibrium adatom density at the step edge. Also, detailed-balance implies that the rate of hopping from the step edge site \( j = 0 \) to sites \( j = \pm 1 \) is given by \( \exp(-\beta \phi_b) h_{\pm} \).

Thus, one has the following discrete steady-state deposition-diffusion equations:

\[
\text{(A.1)} \quad \frac{d}{dt} n(j) = F + h \left[ n(j+1) - 2n(j) - n(j-1) \right] \approx 0 \quad \text{for } j > 1,
\]

\[
\text{(A.2)} \quad \frac{d}{dt} n(1) = F + h \left[ n(2) - n(1) \right] + h_p \left[ n_{EQ} - n(1) \right] + h_p \left[ n(-1) - n(1) \right] \approx 0
\]

with an analogous equation for \( n(-j) \).

A particularly important concept is the idea of smoothly extrapolating or “analytically extending” the values \( n(j) \) of the adatom densities on lower terrace to the right of the step \( (j > 0) \) to an extrapolated value \( n(0+) \) at the step site. This extrapolated value is obtained from the additional equation \([3, 4]\)

\[
\text{(A.3)} \quad \frac{d}{dt} n(1) = F + h \left[ n(2) - 2n(1) + n(0+) \right] = F + h \left[ n(2) - n(1) \right] + h \left[ n(0+) - n(1) \right] \approx 0,
\]

which must be consistent with (A.2). The key point here is that by determining \( n(0+) \) through a generic equation of the form (A.1), one can argue that \( n(0+) \) is a natural or analytic extension of \( n(j) \) for \( j > 0 \). Similarly, one can analytically extend those \( n(j) \) for the upper terrace on the left of the step \( (j < 0) \) to \( n(0-) \). Another perspective is that we define \( n(0+) \) so that the diffusive flux of atoms to the step from the right...
\[ (J_+ \) and left \( (J-) \) satisfy \\
\begin{align*}
J_+ &= h_+ [n(1) - n_{\text{eq}}] + h_p [n(1) - n(-1)] = h [n(1) - n(0+)], \\
J_- &= h_- [n(-1) - n_{\text{eq}}] + h_p [n(-1) - n(1)] = h [n(-1) - n(0-)].
\end{align*}
\]

**Appendix B: Coarse-graining discrete 1D deposition-diffusion equations.** The above discrete 1D model is connected to a coarse-grained continuum model by assuming that the corresponding smooth continuous adatom density per unit length, \( n(x) \), satisfies \( n(x_j = ja) = n_j/a \) at discrete set of spatial points \( x_j \). One then manipulates (A.2) and (A.3) to extract BCs for \( n(x) \) at the step edge \( x = 0 \). The discrete approximation to the right derivative at \( x = 0 \) is
\[ (B.1) \frac{dn}{dx}|_{0^+} \approx \frac{[n(1) - n(0+)]}{a^2}. \]

Thus, comparing (A.2) and (A.3), one obtains
\[ (B.2) D \frac{dn}{dx}|_{0^+} \approx J_+ \quad \text{and} \quad D \frac{dn}{dx}|_{0^-} \approx J_. \]

At this point, one has a choice in formulating BCF type BCs of the type (2). In *one simple formulation*, the \( n_{\pm} \) appearing in (2) are identified with \( n(\pm 1)/a \), and \( n_{\text{eq}} \) with \( n_{\text{eq}}/a \). Then, by comparison of expressions for \( \pm D \frac{dn}{dx}|_{0^\pm} \) with (2), one has that
\[ (B.3) K_{\pm} = ah_{\pm} = D_{\pm}/a = D/L_{\pm} \quad \text{where} \quad L_{\pm} = a \exp(\beta \delta_{\pm}), \]
and \( P = ah_p = D_p/a \) so \( L_p = aD/D_p = ah/h_p \).

However, we argue that a *more appropriate formulation* is to interpret \( n_{\pm} \) as \( n(0\pm)/a \) \cite{4}. This formulation corresponds more closely to the 2D model in this paper where \( n_{\pm} \) are interpreted as densities right at the step edge, but no analytic extension is in fact needed in the 2D model when \( \delta_{\pm} = 0 \). The difference between these two formulations might be regarded as a different assignment of the step edge position. First, consider the simplest case where \( h_p = 0 \) (no permeability). Then, one can solve (B.2) for \( n(1) \) in terms of \( n(0+) \) to obtain
\[ (B.4) n(1) = \frac{h \left[ n(0+) - h_+ n_{\text{eq}} \right]}{(h - h_+)}.
\]

Substituting this result for \( n(1) \) into the right-hand side of (B.2) yields
\[ (B.5) D \frac{dn}{dx}|_{0^+} \approx h \left[ n(0+) - n_{\text{eq}} \right]/(h/h_+ - 1). \]

Thus, replacing \( n(0+) \) by \( n_+/a \) and \( n_{\text{eq}} \) with \( n_{\text{eq}}/a \) yields an expression for \( K_+ \). Together with results of a similar analysis for \( D \frac{dn}{dx}|_{0^-} \), one obtains \cite{4}
\[ (B.6) K_{\pm} = ah/(h/h_{\pm} - 1) = D/L_{\pm}, \quad \text{where} \quad L_{\pm} = a[\exp(\beta \delta_{\pm}) - 1] \quad \text{and} \quad P = 0 \quad \text{(for} \ h_p = 0) \]

For the more general case where \( h_p > 0 \), one might determine both \( n(\pm 1) \) in terms of \( n(0\pm) \) and \( n_{\text{eq}} \). However, some complications arise which we will not discuss in this paper.

**Appendix C: Refined discrete 1D deposition-diffusion models.** It is instructive to introduce a refined version of the discrete 1D deposition-diffusion equation model of Appendix A which more closely reflects the 2D model analyzed in this paper.
Indeed, development of 1D models will generally be most effective if guided by specific 2D models. We retain the geometry of the model described in Appendix A with a 1D array of sites (mimicking rows of sites in 2D) and j=0 denoting the step edge. The key distinction from the standard model is that we now incorporate limited equilibration of the adatom density right at the step edge or “step site,” so that in general \( n(0) \neq 1 \) and \( \exp(-\beta \phi_b) n(0) \neq n_{\text{EQ}} \). See Figure 13. More specifically, we introduce a finite rate, \( R \), for decay of \( n(0) \) to 1. If we do not include direct hopping across the step (i.e., we set \( h_p = 0 \)), then the revised equations become

\[
\frac{d}{dt} n(j) = F + h [n(j+1) - 2n(j) - n(j-1)] \approx 0 \quad \text{for } j > 1,
\]

\[
\frac{d}{dt} n(1) = F + h [n(2) - n(1)] + h_+ [\exp(-\beta \phi_b) n(0) - n(1)] \approx 0,
\]

\[
\frac{d}{dt} n(0) = F + h_+ [n(1) - \exp(-\beta \phi_b) n(0)] + h_- [n(-1) - \exp(-\beta \phi_b) n(0)] + R [1 - n(0)] \approx 0.
\]

With analogous equations for \( n(-j) \). Thus \( R = \infty \) recovers the standard model of Appendix A. We smoothly extrapolate or “analytically extend” the values \( n(j) \) of the adatom densities to the values \( n(0 \pm) \) at the step edge or step site via the defining relations

\[
\frac{d}{dt} n(\pm 1) = F + h [n(\pm 2) - 2n(\pm 1) + n(0 \pm)]
\]

\[
= F + h [n(\pm 2) - n(\pm 1)] + h [n(0 \pm) - n(\pm 1)] \approx 0.
\]

To analyze these equations, it is natural to introduce rescaled densities analogous to the 2D discrete model. One sets \( n^*(j) = n(j) \) for \( j \neq 0 \), \( n^*(0 \pm) = n(0 \pm) \), and \( n^*(0) = \exp(-\beta \phi_b) n(0) \). One then solves the steady-state equations to determine

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**Fig. 13.** Schematic of adatom density in the refined 1D discrete deposition-diffusion model in the vicinity of a step edge. Also shown are the adatom hop rates, the relaxation rate at the step edge, total diffusion fluxes reaching the step edge, \( J_\pm \), the flux across the step due to permeability, \( J_p \), and the flux to the step due to “direct deposition,” \( J_{dd} \).
n*(±1) and n*(0) in terms of n*(0±) and n_{EQ}. Setting r = \exp(\beta \phi_0)R, and using these results to rewrite the expression for the diffusion fluxes approaching the step edge, one obtains

\begin{align}
\text{(C.5)} & \quad K_\pm = a r \left( \frac{h}{h_\pm} - 1 \right)^{-1} \left[ \left( \frac{h}{h_+} - 1 \right)^{-1} + \left( \frac{h}{h_-} - 1 \right)^{-1} + \frac{r}{h} \right]^{-1}, \text{ and} \\
\text{(C.6)} & \quad P = a h \left( \frac{h}{h_+} - 1 \right)^{-1} \left( \frac{h}{h_-} - 1 \right)^{-1} \left[ \left( \frac{h}{h_+} - 1 \right)^{-1} + \left( \frac{h}{h_-} - 1 \right)^{-1} + \frac{r}{h} \right]^{-1}.
\end{align}

### Appendix D: Semicontinuous deposition-diffusion models.

Here, we consider the regime where the kink separation, \(L\), is large and regard the terrace width, \(W\), as fixed. It is natural to replace the fully discrete adatom density \(n(i,j)\) with a \(W\)-dimensional vector \([n(x)\] for \(0 \leq j < W\), where \(n(x) = n(i,j)/a\) denotes the adatom density per unit length along row \(j\). These quantities satisfy a coupled set of continuum deposition-diffusion equations. For an infinite ES barrier, \(\delta_- = 0\), these have the form

\[
\begin{align*}
\frac{\partial}{\partial t} n(x, 1) &= f + D_x \frac{\partial^2}{\partial x^2} n(x, 1) + h \left[ n(x, 2) - \exp(-\beta \phi_\perp) n(x, 1) \right] \approx 0, \\
\frac{\partial}{\partial t} n(x, j) &= f + D_x \frac{\partial^2}{\partial x^2} n(x, j) + h \left[ n(x, j+1) - 2n(x, j) + n(x, j-1) \right] \\
\frac{\partial}{\partial t} n(x, W) &= f + D_x \frac{\partial^2}{\partial x^2} n(x, 1) + h \left[ n(x, W-1) - n(x, W) \right] \approx 0,
\end{align*}
\]

where \(D = a^2 h\) and \(D_x = a^2 h_x\) are diffusion coefficients, and \(f = a - F\) is the deposition rate per unit length. For convenience, we set kink positions at \(x = \pm aL/2\) and solve these equations for \(-aL/2 < x < aL/2\) with BCs \(n(\pm aL/2, j) = 0\) and \(\frac{\partial}{\partial x} n(\pm aL/2, j) = 0\) for \(j > 1\).

Just as for the 2D fully discrete model, it is natural to rescale and shift these densities introducing variables \(\delta n^*(x, 1) = [\exp(-\beta \phi_\perp) n(x, 1) - n_{EQ}]/a\) and \(\delta n^*(x, j) = [n(x, j) - n_{EQ}]/a\) for \(j > 1\), where \(n_{EQ} = \exp(-\beta \phi_0)\). Collecting these variables into a W-dimensional vector \(\delta n^*(x)\), one obtains a steady-state equation of the form

\[
\frac{\partial^2}{\partial x^2} \delta n^*(x) - B(D_x/D, \phi_\perp) \cdot \delta n^*(x) = (f/D) e(D_x/D, \phi_\perp).
\]

The entries in the nonsymmetric \(W \times W\) matrix \(B\) are readily determined from (D.1), as are the entries in the W-component vector \(e\). Solution of the equations is based on determination of a complete biorthonormal set of right- and left-eigenvectors of \(B\) denoted \(\vec{\xi}_k\) and \(\vec{\eta}_k^T\) with eigenvalues \(\lambda_k \geq 0\) for \(0 \leq k \leq W-1\), where \(\vec{\eta}_k \cdot \vec{\xi}_m = \delta_{k,m}\). We will let \(k = 0\) denote the “equilibrium eigenstate” where \(\lambda_0 = 0\). By construction of our scaled variables, the right equilibrium eigenvector \(\vec{\xi}_0\) has equal components (naturally set to unity). The left equilibrium eigenvector \(\vec{\eta}_0\) has a first component equal to \(\exp(-\beta \phi_0) D_x/D\) times the rest.

Setting \(E_k = (f/D) \vec{\eta}_k \cdot \vec{e}\), the solution to (D.2) has the form

\[
\delta n^*(x) = \sum_{0 \leq k \leq W-1} a_k(x) \vec{\eta}_k, \quad \text{where} \quad \frac{\partial^2}{\partial x^2} a_k(x) - \lambda_k a_k(x) = E_k.
\]

Thus, one has

\[
\text{(D.4)} \quad a_0(x) = -1/2E_0 x^2 + b_0 \quad \text{and} \quad a_k(x) = -E_k/\lambda_k + b_k \cosh[(\lambda_k)^{1/2} x] \quad \text{for} \quad k > 0,
\]

already accounting for reflection symmetry about \(x = 0\). The coefficients \(b_k\) are determined by satisfying the BCs. While the detailed forms are complex, the key feature...
is that
\[(D.5)\]
\[b_0 = E_0/L^2/8 + \{b_{k>0} \cosh[(\lambda_k)^{1/2}L/2] \text{ terms}\} \text{ and } b_k \propto L/\sinh[(\lambda_k)^{1/2}L/2] \text{ for } k > 0.\]

Finally reconstructing \(\delta^*(x, 1)\) yields an expression of the form
\[(D.6)\]
\[\delta^*(x, 1) = E_0 \left[ (L/2)^2 - x^2 \right] (v_1)_1 + L \sum_{k>0} \alpha_k [\cosh[(\lambda_k)^{1/2}L/2] - \cosh[(\lambda_k)^{1/2}L/2]]/\sinh(\lambda_k)^{1/2}L/2].\]

Averaging over \(x\) reveals an effective scaling of the excess adatom density at the step edge varying roughly like \(L^2 + BL + C\), as mentioned after (12). The flux approaching the step edge is independent of \(L\) (and is exactly determined as for the fully discrete 2D model). Finally, we mention that the type of analysis and results described here can be readily extended to other cases such as zero attachment barriers, \(\delta_\pm = 0\).

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