

STERIC HINDRANCE OF CRYSTAL GROWTH: NONLINEAR STEP FLOW IN 1+1 DIMENSIONS*

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Abstract. By linking atomistic and mesoscopic scales, we formally show how a local steric effect can hinder crystal growth and lead to a buildup of adsorbed atoms (adatoms) on a supersaturated, (1+1)-dimensional surface. Starting from a many-adatom master equation of a kinetic restricted solid-on-solid (KRSOS) model with *external material deposition*, we heuristically extract a coarse-grained, mesoscale description that defines the motion of a line defect (i.e., a step) in terms of statistical averages over KRSOS microstates. Near thermodynamic equilibrium, we use error estimates to show that this mesoscale picture can *deviate* from the standard Burton–Cabrera–Frank (BCF) step flow model in which the adatom flux at step edges is *linear* in the adatom supersaturation. This deviation is caused by the accumulation of adatoms near the step, which block one another from being incorporated into the crystal lattice. In the mesoscale picture, this deviation manifests as a significant contribution from many-adatom microstates to the corresponding statistical averages. We carry out kinetic Monte Carlo simulations to numerically demonstrate how certain parameters control the aforementioned deviation. From these results, we discuss empirical corrections to the BCF model that amount to a *nonlinear* relation for the adatom flux at the step. We also discuss how this work could be used to understand the kinetic interplay between accumulation of adatoms and step motion in recent experiments of ice surfaces.

Key words. crystal growth, master equation, steric hindrance, kinetic Monte Carlo, step flow, mesoscale limit

AMS subject classifications. 74A50, 82C05, 82C80, 35R35

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1. Introduction. A critical task in materials science has been to understand how atomic defects on crystal surfaces form and evolve, thereby allowing one to assess the stability of novel nanostructures. Below the roughening transition temperature, the growth of nanostructures is mediated by the motion of atomic line defects that resemble steps and act as sources and sinks for adsorbed atoms (adatoms) [5, 21, 11]. By understanding the dynamics of steps, one can therefore also elucidate the morphological evolution of crystal surfaces [16].

A recent experimental observation was that above a critical *supersaturation*, defined as the relative deviation of the adatom density from its equilibrium value, metastable layers of “clustered” adatoms (which are distinct from nucleated islands) populate the surface of ice [23, 3]. It was shown that this metastability is kinetically induced by external material deposition, thereby opening up questions as to the

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precise mechanisms underlying this effect. This observation also raises the following related question: What is the effect on crystal growth of the increased density of adatoms in the vicinity of a step? For a reasonable answer, one must seek links between atomistic dynamics and step motion laws beyond the dilute limit of the adatom gas.

Our goal with this paper is therefore to explore the mesoscopic consequences of a simplified atomistic model for the *nondilute* adatom system via formal asymptotics and numerical simulations. We carry out (i) a formal analysis based on a many-atom master equation for a single-step kinetic restricted solid-on-solid (KRSOS) model in 1+1 dimensions, and (ii) numerical computations via kinetic Monte Carlo (KMC) simulations of the KRSOS model. Importantly, this KRSOS model explicitly includes a steric blocking effect that prevents attachment events when multiple adatoms are near a step. In light of this, we are able to derive *corrections* to a known step flow theory of surface diffusion from exact statistical averages of the master equation.

Our main results are summarized as follows.

- Assuming that a finite number of KRSOS microstates contribute to the system evolution, we derive a formal power-series expansion for the steady-state solution to a master equation with external material deposition.
- By a microscopic averaging in the time-dependent setting, we derive exact expressions for the adatom flux at the step edge. Our formulas separate a linear kinetic law, which becomes exact in the dilute limit of the adatom system [20], from corrections due to steric hindrance near the step edge.
- We find ℓ^∞ -bounds for discrete corrections to the linear kinetic law at the step, and for corrections to a diffusion equation for adatom density on the terrace, when the external deposition flux is sufficiently small. By computing appropriate averages over microscale configurations, we express these error estimates in terms of atomistic parameters of the KRSOS model.
- By carrying out KMC simulations, we describe empirical corrections to the linear theory, particularly a nonlinear (quadratic) relation for the adatom mass flux and the adatom density at the step edge. Furthermore, we empirically determine a condition by which the linear kinetic law for adatom flux at the step is reasonably accurate (see Remark 6.1 in section 6).

Physically, we believe that these results, which link adatom kinetics to step motion, could be used to understand universal mechanisms that contribute to the evolution of crystal surfaces that are not in the dilute regime.

For comparison purposes, we invoke the Burton–Cabrera–Frank (BCF) theory of step flow as a *reference model* for linear kinetics at the step [5]. This model was originally formulated as a phenomenological mesoscale theory for *near-equilibrium* processes that cause steps to move via mass conservation. The principal ingredients are (i) a step velocity law; (ii) the adatom diffusion on terraces, i.e., nanoscale domains bounded by steps; and (iii) a *linear* kinetic law for the density of flux at steps. This model has been enriched to the point where it is now used to describe step flow under an apparently wide range of kinetics on a crystal surface. Nonetheless, basic aspects of step flow remain inadequately understood.

Recently, it was proposed that BCF theory in 1+1 dimensions can be interpreted as a dilute limit of the adatom gas [19, 14]. In this context, the adatom supersaturation is a variable of importance. An emerging issue that we heuristically address in the present work is how supersaturation-driven corrections to the BCF theory can be described consistently with atomistic dynamics on the crystal lattice.

We assume that the reader is familiar with the basic concepts of epitaxial growth.

For broad reviews on the subject, see, e.g., [21, 11, 16].

1.1. Key assumptions and scope. Our starting point is a master equation for the probability density of atomistic configurations. This description, which now includes external material deposition with rate (atoms per unit time) F , is an extension of the deposition-free master equation for adatoms invoked in [20, 19]. Here, one of our tasks is to extract exact statistical averages from the master equation.

Our equation embodies generic rules of the KRSOS model for adatom hopping on terraces (or, the microscopic process for surface diffusion), and detachment and attachment of atoms at the step edge according to detailed balance. In contrast to previous treatments [19, 20], our formalism here also accounts for transitions that *do not conserve* the total mass, or adatom number, as a result of the nonzero F . A simplifying assumption inherent to our formalism is that adatoms do not form bonds away from the step edge and do not interact with each other electrostatically or elastically or by indirect (substrate-mediated) mechanisms; hence, adatom-adatom correlations originate solely from kinetics. The effect of such correlations, particularly the steric blocking of adatom motion, is the main subject of this paper.

The atomistic model allows for the analytical derivation of an exact, closed-form expression for the equilibrium concentration of adatoms on the terrace if $F = 0$. Furthermore, for reasonably arbitrary F , we derive formulas for the adatom fluxes at step edges via formal analysis of the master equation. In this vein, kinetic contributions to the adatom mass flux are manifestly connected to atomistic variables.

We show how, as adatom supersaturation increases, corrections to the linear kinetic law of the BCF model emerge. These corrections are estimated in the ℓ^∞ -sense via perturbations for sufficiently small external deposition flux. Our estimates formally indicate how these corrections can possibly become appreciable when the deposition rate, F , or an Arrhenius factor, k , accounting for bond breaking are large enough to drive the surface to supersaturation.

In addition, by carrying out KMC simulations, we corroborate the analytical findings and characterize these nonlinear corrections for typical values of k and F . Within the mesoscale picture, the adatom fluxes, \mathcal{J}_\pm , toward the step edge are empirically described by an expansion of the form

$$(1.1) \quad \mathcal{J}_\pm \approx c^{eq} \sum_{n=1}^{N_*} \kappa_\pm^{(n)} \bar{\sigma}_\pm^n.$$

In this relation, c^{eq} is the equilibrium (i.e., for $F = 0$) adatom concentration at the step edge, which is computed in closed form here; \mathcal{C}_\pm is the adatom concentration at the upper (−) or lower (+) terrace; $\bar{\sigma}_\pm = \mathcal{C}_\pm/c^{eq} - 1$ is the supersaturation; and $\kappa_\pm^{(n)}$ are kinetic coefficients that in principle depend on atomistic rates. Note that only the $n = 1$ term in (1.1) is present in BCF-type models [11]. Here, we provide evidence for the origin of nonlinear terms in (1.1) and numerically compute the coefficients $\kappa_\pm^{(n)}$ for $n = 1, 2$ via fitting of the KMC data in certain typical cases.

1.2. Past works. It is worthwhile to place our work in the appropriate context of past literature, e.g., [19, 20, 14, 32, 1, 31, 22, 30, 29]. Our goal here is to explore the connection of an atomistic model to mesoscale descriptions of crystals. This theme bears resemblance to the main objectives of [19, 20, 14, 32]. However, in these works [19, 20, 14, 32] the authors' attention focuses on near-equilibrium processes, whereas in the present paper we study the kinetic regime in which external material deposition tends to drive the system away from equilibrium. A similar task is undertaken in [18],

albeit via a (coarse-grained) “terrace-step-kink” model. We herein avoid a priori approximations associated with the diluteness of the adatom system in the vicinity of the step edge; this diluteness is a key, explicit assumption in [19, 20, 14].

Our study here has a perspective distinct from that of [1, 31, 22], in which extensive computations are carried out in 2+1 dimensions. In particular, in [1, 31] the authors derive a set of refined boundary conditions at the step edge that depend on the local environment on the basis of a discrete diffusion equation with a *fixed* step position. In [22] only numerical comparisons of KMC simulations to aspects of the BCF model are shown. A different view is adopted in [30, 29], where a high-dimensional master equation is reduced to a Langevin-type equation for height columns on the crystal lattice. We should also mention the probabilistic approach in [15] for the passage from an atomistic description within a solid-on-solid model to a *fully* continuum picture.

A discussion that the boundary condition involving the mass flux toward the step edge may exhibit a nonlinear behavior as a function of the adatom density can be found in [4, 7]. Specifically, in [4] the authors carry out numerical simulations of a “terrace-step-kink” model that reveal a nonlinear dependence of adatom fluxes on the supersaturation, $\bar{\sigma}_{\pm}$, and relate this behavior to the step-continuum thermodynamic approach of [7].

In the present treatment, we point out such a nonlinearity at the mesoscale from a kinetic atomistic perspective, avoiding continuum thermodynamic principles. By recourse to atomistic mechanisms, we argue that nonlinear terms in the boundary conditions for the mass flux naturally emerge as the system is driven farther from equilibrium; cf. (6.2). Our long-term goal is to address phenomena in two-dimensional (2D) settings, for which atomistic models with kinks have been proposed [6].

1.3. Limitations. Notably, our atomistic model is one-dimensional (1D). This simplification has some unphysical consequences. For example, the model leaves out surface features intimately connected to the effect of step stiffness or curvature [5]. In an effort to single out the hindrance effect that the accumulation of adatoms has on step flow locally, we neglect nucleation [27]. Mathematically, this assumption simplifies tracking down the step position analytically (since no additional steps are formed). Physically, our assumption that islands do not nucleate may be justified as follows. As pointed out in [20], in the 1D setting nearest-neighbor bonds of adatoms can lead to kinetic steady states in which the probability of an island nucleating is independent of its size. However, in 2D settings, Boltzmann statistics imply the dependence of this probability on the island size. Our assumption that adatoms do not bond renders the analysis more consistent with 2D systems while avoiding subtleties associated with 1D nucleation. Furthermore, we focus on the motion of a single step. This consideration leaves out elastic step-step interactions [11, 21]. The issue of stochastic fluctuations in step motion lies beyond our present scope; see [14] for a discussion of this effect in a kinetic regime near the dilute limit for adatoms.

1.4. Outline. The remainder of the paper is organized as follows. Section 2 provides a review of the main models: the atomistic KRSOS model (section 2.1), which is the starting point of our analysis; and a BCF-type model of step flow in 1D (section 2.2), which serves as a reference model for the mesoscale picture. In section 3, we calculate the steady-state solution for the master equation of the KRSOS model with material deposition onto the surface from above (sections 3.1 and 3.2) and show a useful property of the time-dependent solution to a marginalized version of the master equation (section 3.3). Exact statistical averages of the KRSOS model, which imply

a modified discrete BCF-type model, are developed in section 4. By this formalism, in section 5 we heuristically derive bounds for corrections to the discrete, linear BCF-type laws (section 5.1) and thereby extract the continuum BCF-type model (section 5.2). In section 6, we characterize high-supersaturation corrections for the mass flux at the step edge via KMC simulations and propose a more general kinetic relation for mesoscale step flow models. Section 7 contains a summary and discussion of our results—particularly their relevance to recent laboratory experiments.

Notation. We write $f = \mathcal{O}(g)$ ($f = o(g)$) to imply that $|f/g|$ is bounded by a nonzero constant (approaches zero) in a prescribed limit. We write $f = \mathcal{O}(h, g)$ to imply a relation of the form $f = \mathcal{O}(h) + \mathcal{O}(g)$. We use the symbol \lesssim to denote boundedness up to the constant factor. The symbol \mathbb{R} denotes the set of reals.

2. Background: Atomistic and mesoscale models. In this section, we describe ingredients of the atomistic and mesoscale models, which form the core of our paper. In particular, we introduce the master equation of atomistic dynamics with material deposition onto the surface from above and review basics of the BCF model.

2.1. Microscale: KRSOS model. At the microscale, we consider a simple-cubic crystal surface with a single step [20]. The surface consists of distinct height columns on a 1D lattice of lateral spacing a , with total length $L = Na$; see Figure 1. We consider $L = \mathcal{O}(1)$ as $a \rightarrow 0$, e.g., by setting $L = 1$. Screw-periodic boundary conditions are applied in the x -direction.

Atoms of the top layer that have two in-plane nearest neighbors are *step atoms*; these atoms are immobile in our model [20]. In contrast, the atom of the step edge, which lies at one end of the top layer, has a single in-plane nearest neighbor and is referred to as an *edge atom*; it may detach from the step and move to one of the adjacent terraces. By this picture, the adatoms are movable atoms that are neither edge atoms nor step atoms [20].

In our model, we do not allow islands to form; thus, if any two adatoms become nearest neighbors on a terrace, they do not form a bond with each other. Adatoms are free to diffuse across the surface until they reach the step, which acts as a sink or source of them. Externally deposited atoms are assumed to become adatoms on the terrace instantly and may not attach to the step directly [14].

2.1.1. On atomistic processes and system representation. Our model is characterized by transitions between discrete configurations of adatoms. The total mass of these configurations is *not* conserved if $F \neq 0$, in contrast to the setting in [20]. The transitions are controlled by F as well as by Arrhenius rates which have the form $\nu \exp[-E/(k_B T)]$, where ν is an attempt frequency, T is the absolute temperature, k_B is Boltzmann constant, and E is an appropriate activation energy [20].

The basic processes allowed by our 1D atomistic model are shown in Figure 1. The requisite atomistic rates can be described as follows [20]. First, the rate $D = \nu \exp[-E_h/(k_B T)]$ accounts for unbiased adatom hopping on terraces, sufficiently away from a step edge. The extra factor $\phi_{\pm} = \exp[-E_{\pm}/(k_B T)]$ expresses additional energy barriers, E_{\pm} , corresponding to adatom attachment to the step edge from the lower (+) or upper (−) terrace. Finally, the factor $k = \exp[-E_b/(k_B T)]$ accounts for the extra energy, E_b , that is necessary for the breaking of the edge-atom bonds with step atoms so that the atom detaches from the step edge.

In principle, our 1D system can have a (countably) infinite number of adatom configurations under the influence of a nonzero deposition, F . We are compelled to represent such atomistic configurations by *multisets* [20]. A multiset, α , is an

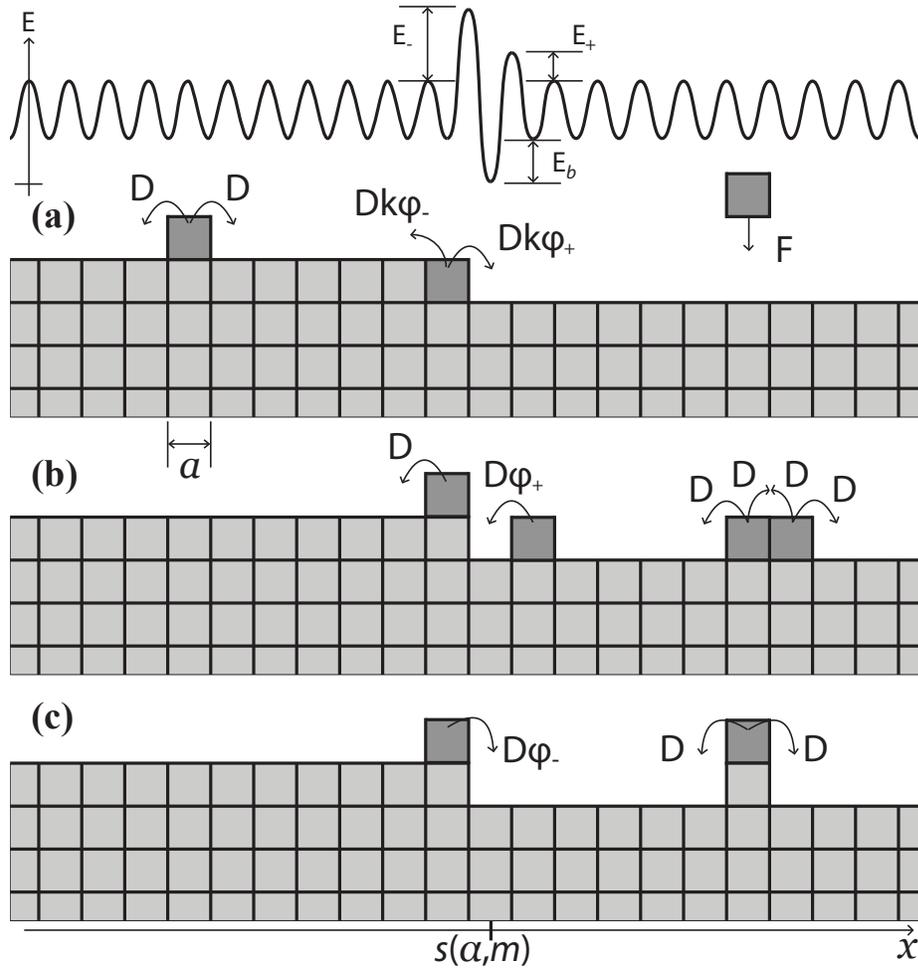


FIG. 1. Microscopic view: Schematic of atomistic processes allowed by the 1D atomistic model on a lattice with lateral spacing a . Movable atoms (adatoms) are shown in dark grey. (a) Top panel: Hopping of adatoms on each terrace with rate D , detachment of edge atom from step to upper ($-$) or lower ($+$) terrace with rate $Dk\phi_{\pm}$, and deposition of atoms from above with rate F . The deposited atom becomes an adatom instantly. (b) Middle panel: Hopping of adatom at step to same terrace with rate D , attachment of adatom from lower terrace to step edge with rate $D\phi_+$, and hopping of (unbonded) adatoms forming a pair with rate D . Adatoms cannot form islands. (c) Bottom panel: Attachment of adatom from upper terrace to step edge with rate $D\phi_-$, and hopping of adatom lying on top of another adatom to same terrace with rate D . The site to the right of the step is labeled $s(\alpha, m)$; see Definition 2.2.

unordered list whose entries correspond to the positions of adatoms on the 1D lattice; in particular, $\alpha = \{\}$ expresses a configuration that is void of adatoms. Departing from [20], we use multisets α containing the Lagrangian coordinates of adatoms. For notational clarity, the indices i and j label lattice sites in a fixed (Eulerian) coordinate system, whereas \hat{i} and \hat{j} label sites in a (Lagrangian) coordinate frame relative to the step. Accordingly, repeated entries in α indicate multiple adatoms occupying the same lattice site. For example, the system configuration represented by $\alpha = \{\hat{i}, \hat{j}, \hat{j}\}$ has one adatom at site \hat{i} and two adatoms at site \hat{j} . The number of adatoms corresponding to

α is simply $|\alpha|$, the cardinality of the multiset.

In connecting the atomistic model to one-step flow with $F = 0$ in 1D, our approach relies on explicitly determining the position of the step edge at time $t > 0$ from the number of adatoms, $|\alpha|$, and the initial adatom configuration [20]. This is a consequence of mass conservation. If $F \neq 0$, however, more information is needed in order to track the step edge: At every atomistic transition, one must account for the atoms deposited from above.

For our purposes, a system representation that allows this bookkeeping results from using an integer, m , in addition to using α . This m is the total *mass*, or number of atoms, of the system. Given the initial position, s_0 , of the site to the right of the step edge in a fixed (Eulerian) coordinate system, we can explicitly track the step for all time $t > 0$.

DEFINITION 2.1 (representation of atomistic system). *The pair (α, m) defines the state of the atomistic system: the multiset α expresses the adatom configuration, and the index m is an integer that counts the overall mass of the system. Thus, if m_0 is the initial mass, then $m - m_0$ counts how many adatoms are deposited on the surface from above.*

DEFINITION 2.2 (discrete step position). *For each state (α, m) , the discrete step position in Eulerian coordinates is $s(\alpha, m) = s_0 - |\alpha| + m - m_0$. Accordingly, $s(\alpha, m)$ references the site to the right of the step edge; see Figure 1.*

2.1.2. Master equation and marginalized version. The KRSOS model is described by a time-dependent probability density function (PDF), $p_{\alpha, m}(t)$, defined over the domain of discrete states (α, m) . Hence, the time evolution of the system is governed by the master equation

$$(2.1) \quad \dot{p}_{\alpha, m}(t) = \sum_{\alpha', m'} T_{(\alpha, m), (\alpha', m')} p_{\alpha', m'}(t),$$

under given initial data, $p_{\alpha, m}(0)$. In the above, $T_{(\alpha, m), (\alpha', m')}$ expresses the overall transition of the system from state (α', m') to state (α, m) . Evidently, master equation (2.1) governs a Markov process with countably infinite states.

Next, we describe the rates $T_{(\alpha, m), (\alpha', m')}$. The nonzero transition rates obey the following rules:

$$(2.2a) \quad T_{(\alpha, m), (\alpha', m')} = D \quad \text{if } m = m' \text{ and } |\alpha| = |\alpha'| \text{ and } |\alpha \setminus \alpha'| = 1 \\ \text{and } \left| \|\alpha \setminus \alpha'\| - \|\alpha' \setminus \alpha\| \right| = 1;$$

$$(2.2b) \quad T_{(\alpha, m), (\alpha', m')} = D\phi_{\pm} \quad \text{if } m = m' \text{ and } |\alpha| = |\alpha'| - 1 \\ \text{and } \alpha' \setminus \tilde{\alpha} = \{\pm 1\};$$

$$(2.2c) \quad T_{(\alpha, m), (\alpha', m')} = Dk\phi_{\pm} \quad \text{if } m = m' \text{ and } |\alpha| = |\alpha'| + 1 \\ \text{and } \alpha \setminus \tilde{\alpha}' = \{\pm 1\};$$

$$(2.2d) \quad T_{(\alpha, m), (\alpha', m')} = \frac{F}{N-1} \quad \text{if } m = m' + 1 \text{ and } |\alpha| = |\alpha'| + 1 \\ \text{and } |\alpha \setminus \alpha'| = 1;$$

and, so that probability is conserved,

$$(2.2e) \quad T_{(\alpha', m'), (\alpha', m')} = - \sum_{\substack{(\alpha, m) \\ (\alpha, m) \neq (\alpha', m')}} T_{(\alpha, m), (\alpha', m')} \quad \text{for all } (\alpha', m').$$

All transition rates not listed in (2.2) are zero. Here, we introduce the multiset difference $\alpha \setminus \alpha'$, which itself is a multiset containing the elements in α that are not in α' , counting multiplicity. For example, $\{\hat{i}, \hat{j}, \hat{j}\} \setminus \{\hat{j}\} = \{\hat{i}, \hat{j}\}$. Additionally, the symbol $\|\cdot\|$ indicates the ℓ^p -norm with $p \geq 1$, and we define the “multiset increment operation” as $\tilde{\alpha} = \{\hat{i} + 1\}$ for all $\hat{i} \in \alpha$; i.e., the set $\tilde{\alpha}$ is just α after each element has been incremented by one. Setting $F = 0$ in (2.2) reduces (2.1) to the master equation governing surface relaxation [20].

Among the transition rates that are zero, notable examples include

$$\begin{aligned}
 (2.3a) \quad T_{(\alpha,m),(\alpha',m')} &= 0 && \text{if } m = m' \text{ and } |\alpha| < |\alpha'| - 1 \text{ or } |\alpha| > |\alpha'| + 1; \\
 T_{(\alpha,m),(\alpha',m')} &= 0 && \text{if } m = m' \text{ and } |\alpha| = |\alpha'| + 1 \\
 (2.3b) &&& \text{and } -1 \in \alpha'; \\
 (2.3c) \quad T_{(\alpha,m),(\alpha',m')} &= 0 && \text{if } m = m' + 1 \text{ and } |\alpha| \leq |\alpha'|.
 \end{aligned}$$

Equation (2.3a) indicates that no more than one atom may attach to or detach from the step in a single transition. Equation (2.3b) asserts that no atoms may detach if the site directly above the edge atom is occupied, and (2.3c) prevents atoms from being deposited at $s(\alpha, m)$. Note that the transitions described in (2.2a)–(2.2c), along with (2.3a) and (2.3b), are subject to detailed balance [14, 20]. Our definition of rates $T_{(\alpha,m),(\alpha',m')}$ here accounts for both gain and loss terms for $p_{\alpha,m}(t)$ in master equation (2.1); cf. (2.2e).

Master equation (2.1) along with transition rates (2.2) and (2.3) completely governs the full mass-dependent microscale model. For some of our purposes, notably Proposition 3.1 and its application, we require an alternate version of (2.1) that describes the evolution of a marginal PDF, $p_{\alpha}(t)$, where the mass variable, m , has been summed out.

DEFINITION 2.3 (marginal PDF). *The marginal probability density is*

$$(2.4) \quad p_{\alpha}(t) = \sum_m p_{\alpha,m}(t),$$

where $p_{\alpha,m}(t)$ satisfies (2.1) with transition rates (2.2) and (2.3).

The marginal PDF of this definition satisfies what will be referred to as the marginalized master equation, found by summing over the mass variable m on both sides of (2.1); cf. (2.5). It is important to note that a sum over m on the right-hand side of master equation (2.1) involves careful consideration of rules (2.2) since the transition rates $T_{(\alpha,m),(\alpha',m')}$ depend on m in addition to $p_{\alpha,m}(t)$.

The marginalized master equation is

$$\begin{aligned}
 (2.5) \quad \dot{p}_{\alpha}(t) &= \sum_{\alpha'} T_{\alpha,\alpha'} p_{\alpha'}(t) \\
 &= D \sum_{\alpha'} [A_{\alpha,\alpha'} + \epsilon B_{\alpha,\alpha'}] p_{\alpha'}(t).
 \end{aligned}$$

Here, $A_{\alpha,\alpha'}$ accounts for the atomistic processes of attachment and detachment at the step edge, and atom hopping on each terrace, as described in [20]; and $B_{\alpha,\alpha'}$ together with the nondimensional parameter $\epsilon \equiv F/D$ accounts for material deposition onto the surface from above. In (2.5), ϵ plays the role of a Péclet number, measuring the deposition rate relative to terrace diffusion. Note that the symbol R has previously been used for the inverse ratio, $R = D/F$, in part of the physics literature [2].

The scaled, nonzero transition rates $A_{\alpha, \alpha'}$ and $B_{\alpha, \alpha'}$ can be described by rules similar to those in (2.2), viz.,

$$\begin{aligned}
 A_{\alpha, \alpha'} &= 1 && \text{if } |\alpha| = |\alpha'| \text{ and } |\alpha \setminus \alpha'| = 1 \text{ and} \\
 & && \left| \|\alpha \setminus \alpha'\| - \|\alpha' \setminus \alpha\| \right| = 1; \\
 A_{\alpha, \alpha'} &= \phi_{\pm} && \text{if } |\alpha| = |\alpha'| - 1 \text{ and } \alpha' \setminus \tilde{\alpha} = \{\pm 1\}; \\
 A_{\alpha, \alpha'} &= k\phi_{\pm} && \text{if } |\alpha| = |\alpha'| + 1 \text{ and } \alpha \setminus \tilde{\alpha}' = \{\pm 1\}; \\
 B_{\alpha, \alpha'} &= \frac{1}{N-1} && \text{if } |\alpha| = |\alpha'| + 1 \text{ and } |\alpha \setminus \alpha'| = 1; \\
 (2.6) \quad A_{\alpha', \alpha'} &= - \sum_{\substack{\alpha \\ \alpha \neq \alpha'}} A_{\alpha, \alpha'}, && B_{\alpha', \alpha'} = - \sum_{\substack{\alpha \\ \alpha \neq \alpha'}} B_{\alpha, \alpha'} \quad \text{for all } \alpha'.
 \end{aligned}$$

One may view master equation (2.5) as a kinetic hierarchy of coupled particle equations for adatoms. For a fixed number of adatoms, $|\alpha| = n$, a combinatorial argument entails that there are

$$(2.7) \quad \omega(n) = \binom{n + N - 2}{n}$$

distinct atomistic configurations on the 1D lattice of size N ($N \geq 2$). By (2.7), $\ln \omega(n)$ grows as $\mathcal{O}(n)$ for $n \gg 1$ with $n = \mathcal{O}(N)$. Evidently, situations with high enough supersaturation imply the contribution to p_{α} from states that have many adatoms, i.e., large $|\alpha|$. In [20, 19] this complication is avoided by restricting our attention to the dilute regime, in which the dynamics of (2.5) are dominated primarily by 0- and 1-particle states. In the present work, we aim to account for higher particle states, thus transcending the dilute regime of the adatom gas assumed in [20, 19]. Unless we state otherwise, we assume that the number of adatoms cannot exceed a certain bound, M : $|\alpha| \leq M$, where M is a fixed yet arbitrary positive integer.

2.2. Mesoscale: BCF model. By phenomenology, the BCF model treats adatoms and the crystal surface in a continuum fashion in the lateral direction, yet retains the atomistic detail of the crystal in the vertical direction [5, 11]. This approach makes use of an adatom concentration, ρ , on each terrace in the laboratory frame. To simplify the model without losing sight of the essential physics, we assume that the desorption and evaporation of atoms is negligible. (It should be noted, however, that desorption is treated by BCF [5].)

The geometry of a step adjoining two terraces is depicted in Figure 2. The upper (−) terrace, on the left of the step edge, and lower (+) terrace, on the right of the step edge, differ in height by a' , an atomic length. In this view, the adatoms are represented by the concentration field $\rho(x, t)$. Let $\zeta(t)$ be the position of the step edge. We apply screw-periodic boundary conditions in the spatial coordinate, x .

The step velocity, $v(t) = \dot{\zeta}(t)$, is determined by mass conservation:

$$(2.8) \quad v = \frac{\Omega}{a'} (J_- - J_+),$$

where J_{\pm} denotes the x -directed mass flux at the step edge on the upper (−) or lower (+) terrace, $\Omega = aa'$ is the atomic area, and a is the lattice spacing in the lateral (x -) direction.

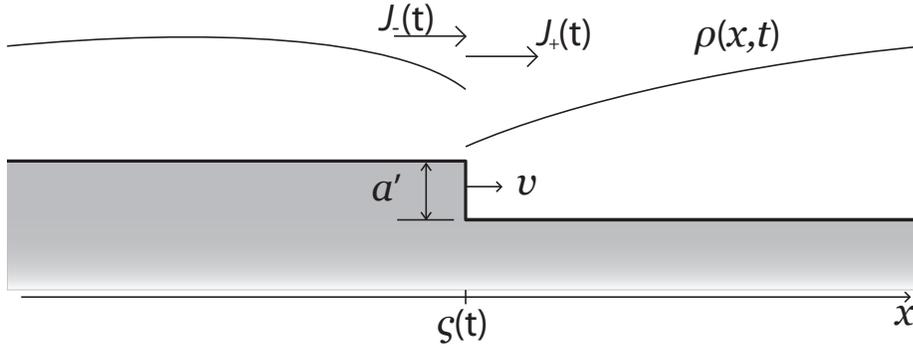


FIG. 2. Mesoscale view: Schematic of a step with atomic height a' adjoining two terraces. The dependent variable $\rho(x, t)$ is the adatom concentration field on each terrace in the laboratory frame. The step velocity, $v = \dot{\zeta}(t)$, is determined by the adatom fluxes J_{\pm} at the step edge on the lower (+) or upper (−) terrace via mass conservation; cf. (2.8).

For later algebraic convenience, we define $\hat{x} := x - \zeta(t)$, which is the coordinate relative to the step edge. On each terrace, the variable $\mathcal{C}(\hat{x}, t) = \rho(x, t)$ satisfies [5]

$$(2.9) \quad \frac{\partial \mathcal{C}}{\partial t} = \mathcal{D} \frac{\partial^2 \mathcal{C}}{\partial \hat{x}^2} + v \frac{\partial \mathcal{C}}{\partial \hat{x}} + \mathcal{F},$$

where \mathcal{D} is the macroscopic adatom diffusivity and \mathcal{F} is the mesoscopic external deposition flux [21, 11]. Note the presence of the advection term, $v(\partial \mathcal{C} / \partial \hat{x})$, on the right-hand side of (2.9); this term originates from $\partial \rho / \partial t$ in the corresponding diffusion equation for $\rho(x, t)$, viz., $\partial \rho / \partial t = \mathcal{D}(\partial^2 \rho / \partial x^2) + \mathcal{F}$. Thus, the flux at the step edge consistent with Fick’s law is

$$(2.10) \quad J_{\pm} = -\mathcal{D}(\partial \mathcal{C} / \partial \hat{x})_{\pm} - v \mathcal{C}_{\pm} = -\mathcal{D}(\partial \rho / \partial x)_{\pm} - v \rho_{\pm}.$$

The remaining ingredient of the BCF model is a set of boundary conditions for \mathcal{C} , or ρ , at the step edge through the mass flux, $J(x, t)$. Burton, Cabrera, and Frank originally introduced Dirichlet boundary conditions, by which the restriction \mathcal{C}_{\pm} of \mathcal{C} at the step edge is set equal to an equilibrium value, c^{eq} [5]. Later on, a Robin boundary condition was imposed [8] via the linear version of condition (1.1). This condition was later improved by incorporation of the Ehrlich–Schwoebel barrier [9, 26]. The linear kinetic relation for the mass flux at the step is

$$(2.11) \quad J_{\pm} = \mp \kappa_{\pm} (\mathcal{C}_{\pm} - c^{eq}),$$

where κ_{\pm} describes the rate of attachment/detachment of atoms at the step in the presence of an Ehrlich–Schwoebel barrier.

In [4], numerical simulations based on a “terrace-step-kink” model suggest a nonlinear dependence of J_{\pm} on $\mathcal{C}_{\pm} - c^{eq}$. The authors argue that this can be explained by the thermodynamic approach of [7]. The observation of such a nonlinear effect motivates us to conjecture a generalized relation of form (1.1), where the terms corresponding to $n \geq 2$ account for far-from-equilibrium, high-supersaturation corrections to the traditional linear kinetic law (2.11). In section 4, we provide evidence for corrections to (2.11) that emerge from kinetic aspects of our 1D atomistic model.

3. KRSOS model: Analytical properties. In this section, we point out significant properties of the KRSOS model. Without external material deposition, for

$F = 0$, the steady-state solution to master equation (2.1) is known to correspond to the equilibrium distribution of adatoms [20]. First, we derive an exact, closed-form expression for this equilibrium solution via the canonical ensemble [10] (section 3.1). We also discuss the steady-state solution of marginalized master equation (2.5) for sufficiently small F , $F \neq 0$, by assuming that a finite number of particle states contribute to the governing kinetic hierarchy (section 3.2). Finally, we state and prove a property of the time-dependent solution to (2.5), which forms an extension of the “maximum principle” introduced in [20] (section 3.3).

3.1. Equilibrium distribution, $F = 0$ ($\epsilon = 0$). We will assume that the system is initially in a state whose mass is m_0 with probability equal to unity. Then, the use of mass index m for states of the KRSOS model is unnecessary since $m = m_0$ for all time $t > 0$. In this situation, the full master equation (2.1) is equivalent to the marginalized master equation (2.5). We will refer to the latter equation in this case with $\epsilon = 0$.

When external deposition is absent, master equation (2.5) has an equilibrium solution, p_{α}^{eq} , by Kolmogorov’s criterion [20]. This equilibrium solution was given in [20] by recourse to the canonical ensemble of statistical mechanics. We will now improve the result of [20] by representing p_{α}^{eq} in simple closed form.

Recall that $Dk\phi_{\pm}$ is the detachment rate, where $k = \exp[-E_b/(k_B T)]$, and E_b measures the energy of the adatom resulting from detachment of an edge atom.

In the KRSOS model, the energy of each adatom configuration, α , is simply $|\alpha|E_b$. By applying the Boltzmann–Gibbs distribution at equilibrium, we can assert that the probability of having n adatoms is $\text{Prob}\{|\alpha| = n\} = c \exp[-nE_b/(k_B T)]$, where c is a normalization constant. Consequently, the partition function, Z , for adatoms is computed as [10]

$$\begin{aligned} Z &= \sum_{\alpha} e^{-|\alpha|E_b/(k_B T)} \\ (3.1) \quad &= \sum_{n=0}^{\infty} \omega(n) e^{-nE_b/(k_B T)} = \frac{1}{(1-k)^{N-1}}, \end{aligned}$$

by using (2.7) and the binomial expansion. Thus, the equilibrium solution is

$$(3.2) \quad p_{\alpha}^{eq} = \frac{1}{Z} e^{-|\alpha|E_b/T} = (1-k)^{N-1} k^{|\alpha|}.$$

Notice that $p_{\alpha}^{eq} \propto k^{|\alpha|}$ if $Nk \ll 1$; cf. [20].

3.2. Steady state of atomistic model with $F > 0$. In this subsection, we discuss a plausible steady-state solution of our KRSOS model for sufficiently small ϵ ($\epsilon = F/D$). To this end, we employ a formal argument based on the assumption that only a finite number of particle (adatom) states contribute to the system evolution; $|\alpha| \leq M$ for arbitrary yet fixed M .

In contrast to the case with $F = 0$, for which the Kolmogorov criterion holds and entails the existence of the equilibrium solution [20], microscopic reversibility is lost for nonzero deposition flux, $F > 0$. In fact, by use of a known kinetic model, in Appendix A we show that no steady-state solution of master equation (2.5) exists in the kinetic regime with $\epsilon > \phi_+ + \phi_-$. This latter condition implies that the external deposition rate is larger than the rate of attachment; consequently, from a physical viewpoint, a steady accumulation of adatoms on the terrace can occur for long enough times.

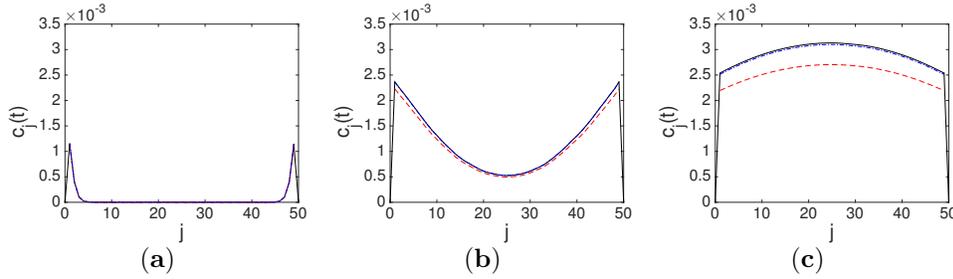


FIG. 3. (Color available online.) Snapshots of the number, $c_j(t)$, of adatoms per lattice site, j , versus j (Lagrangian coordinate) for fixed time, t , by KMC simulations, with $N = 50$, $D = 10^{10} \text{ sec}^{-1}$, $k = 2.5 \times 10^{-3}$, $\phi_{\pm} = 1$, and $F = 10^7 \text{ sec}^{-1}$ ($\epsilon = 10^{-3}$). The time of simulation increases from left to right: (a) $t = 10^{-10}$; (b) $t = 10^{-8}$; and (c) $t = 10^{-6}$. In each plot, the red dashed curve shows the contribution to $c_j(t)$ from 1-particle states; the blue dash-dot curve includes both 1- and 2-particle states; and the black solid curve is the overall adatom number density. The standard deviation of densities in 10 ensembles of 10^6 simulations estimates errors smaller than the thickness of the plotted curves.

In the remainder of this subsection, we make the conjecture (but do not prove) that a finite number of particle states contribute to the system evolution. Accordingly, we restrict our attention to the kinetic regime with sufficiently small ϵ ($\epsilon \ll 1$). Our conjecture is favored by KMC simulations, a sample of which is shown in Figure 3.

By enforcement of restriction $|\alpha| \leq M$, master equation (2.5) reduces to

$$\begin{aligned} \dot{\mathbf{p}}^\epsilon(t) &= \mathfrak{T}\mathbf{p}^\epsilon(t) \\ (3.3) \quad &= D(\mathfrak{A} + \epsilon\mathfrak{B})\mathbf{p}^\epsilon(t), \end{aligned}$$

where \mathbf{p}^ϵ is the ϵ -dependent vector of dimension $\Omega(M) := \sum_{n=0}^M \omega(n) = (M + N - 1)!/[M!(N - 1)!]$ formed by p_α , and the \mathfrak{T} matrix is split into the (finite-dimensional) attachment/detachment matrix, \mathfrak{A} , and deposition matrix, $\epsilon\mathfrak{B}$, in correspondence to the $A_{\alpha,\alpha'}$ and $\epsilon B_{\alpha,\alpha'}$ of (2.2). We impose the ϵ -independent initial data $\mathbf{p}(0) =: \mathbf{p}_0$.

The approximation of the full microscopic model by (3.3) offers two obvious advantages. First, the time-dependent solution of (3.3) can be expressed conveniently in terms of a matrix exponential. Second, the unique steady-state distribution of (3.3) always exists; it is the normalized eigenvector of the \mathfrak{T} matrix with zero eigenvalue [12].

We proceed to formally express the steady-state solution, $\mathbf{p}^{ss,\epsilon}$, of (3.3) as an appropriate series expansion in ϵ . This task can be carried out in several ways—for example, through the conversion of (3.3) to a Volterra integral equation, an approach that we choose to apply here. By treating $\epsilon D\mathfrak{B}\mathbf{p}^\epsilon(t)$ as a forcing term in (3.3), the method of variation of parameters yields

$$(3.4) \quad \mathbf{p}^\epsilon(t) = \Phi(t) \left[\mathbf{p}_0 + \epsilon D \int_0^t \Phi^{-1}(t') \mathfrak{B}\mathbf{p}^\epsilon(t') dt' \right],$$

where $\Phi(t) := \exp(D\mathfrak{A}t)$. We mention in passing that, by the usual theory of Volterra equations, (3.4) has a unique solution locally in time [28].

The matrix \mathfrak{A} is diagonalizable because it corresponds to the transition matrix of a Markov process satisfying detailed balance [12]. Thus, we apply the decomposition $\mathfrak{A} = V\Lambda V^{-1}$ where $\Lambda = \text{diag}\{\lambda_j\}_{j=1}^{\Omega(M)}$, $\{\lambda_j\}$ are the (nondimensional) eigenvalues of \mathfrak{A} , and V is a matrix whose column vectors are the respective eigenvectors. Let $\{\lambda_j\}_{j=1}^{\Omega(M)}$ be ordered, $0 = \lambda_1 > \lambda_2 \geq \dots \geq \lambda_{\Omega(M)}$ [12]. By $\Phi(t) = Ve^{Dt\Lambda}V^{-1}$, we

have $\Phi^{-1}(t) = Ve^{-Dt\Lambda}V^{-1}$. Hence, (3.4) is recast to

$$(3.5) \quad \mathbf{p}^\epsilon(t) = Ve^{Dt\Lambda}V^{-1}\mathbf{p}_0 + \epsilon D \int_0^t Ve^{D(t-t')\Lambda}V^{-1}\mathfrak{B}\mathbf{p}^\epsilon(t')dt'.$$

At this stage, a formula for $\mathbf{p}^\epsilon(t)$ ensues by standard methods. We resort to the Laplace transform, $\widehat{\mathbf{p}}^\epsilon(s) = \int_0^\infty e^{-st}\mathbf{p}^\epsilon(t)dt$, of $\mathbf{p}^\epsilon(t)$ with $\text{Res} > c > 0$ for some suitable positive number c ; by (3.5), we directly obtain

$$(3.6) \quad \widehat{\mathbf{p}}^\epsilon(s) = [I - \epsilon D V \mathfrak{D}(s) V^{-1} \mathfrak{B}]^{-1} V \mathfrak{D}(s) V^{-1} \mathbf{p}_0,$$

where $\mathfrak{D}(s) := \text{diag}\{(s - D\lambda_j)^{-1}\}_{j=1}^{\Omega(M)}$ and I is the unit matrix. In (3.6), we assume that ϵ is small enough so that the requisite inverse matrix makes sense.

The next step in this approach is to compute the inverse transform of (3.6). However, in principle, this choice requires carrying out in the right half of the s -plane the inversion of the matrix $I - \epsilon D V \mathfrak{D}(s) V^{-1} \mathfrak{B}$ for arbitrary M . This task is considerably simplified for the steady-state solution, $\mathbf{p}^{ss,\epsilon}$, in the limit $t \rightarrow \infty$, as shown in Appendix B. The resulting formula reads

$$(3.7) \quad \mathbf{p}^{ss,\epsilon} = \mathbf{p}^0 + \sum_{l=1}^{\infty} (-\epsilon \mathfrak{A}^\dagger \mathfrak{B})^l \mathbf{p}^0.$$

In the above, \mathbf{p}^0 corresponds to the equilibrium solution in the absence of external deposition ($\epsilon = 0$), and \mathfrak{A}^\dagger denotes the Moore–Penrose pseudoinverse of \mathfrak{A} . Equation (3.7) indicates the relative contributions of external deposition and diffusion and attachment/detachment processes to the steady state of the assumed M -particle KR-SOS model underlying this calculation.

Our heuristics leave several open questions regarding the meaning of (3.7) for large particle number M . For instance, the behavior with M of the bound for ϵ needed for convergence has not been addressed. A related issue is to estimate the error by the truncation of series (3.7), after a finite number of terms are summed.

3.3. Property of marginalized master equation. Now consider marginalized master equation (2.5) with $\epsilon \geq 0$.

PROPOSITION 3.1. *If a nontrivial steady-state solution, p_α^{ss} , of (2.5) exists, then any solution $p_\alpha(t)$ satisfies*

$$(3.8) \quad \max_\alpha \frac{p_\alpha(t)}{p_\alpha^{ss}} \leq \max_\alpha \frac{p_\alpha(0)}{p_\alpha^{ss}}, \quad t > 0.$$

We proceed to prove Proposition 3.1 by invoking the identity

$$(3.9) \quad \sum_{\alpha'} T_{\alpha,\alpha'} p_{\alpha'}^{ss} = 0,$$

which follows directly from the definition of p_α^{ss} .

Proof. Equation (2.5) can be written as

$$\begin{aligned}
 \dot{p}_\alpha(t) &= \sum_{\alpha'} T_{\alpha, \alpha'} p_{\alpha', m'}(t) \\
 &= T_{\alpha, \alpha} p_\alpha(t) + \sum_{\alpha' \neq \alpha} T_{\alpha, \alpha'} p_{\alpha'}(t) \\
 &= T_{\alpha, \alpha} p_\alpha^{ss} \frac{p_\alpha(t)}{p_\alpha^{ss}} + \sum_{\alpha' \neq \alpha} T_{\alpha, \alpha'} p_{\alpha'}^{ss} \frac{p_{\alpha'}(t)}{p_{\alpha'}^{ss}} \\
 (3.10) \qquad &= \sum_{\alpha' \neq \alpha} T_{\alpha, \alpha'} p_{\alpha'}^{ss} \left\{ \frac{p_{\alpha'}(t)}{p_{\alpha'}^{ss}} - \frac{p_\alpha(t)}{p_\alpha^{ss}} \right\}.
 \end{aligned}$$

Note that $T_{\alpha, \alpha'} p_{\alpha'}^{ss} \geq 0$ for all $\alpha' \neq \alpha$. Thus, the sign of $\dot{p}_\alpha(t)$ is determined by the quantity in brackets. In particular, if α maximizes (minimizes) $p_{\alpha'}(t)/p_{\alpha'}^{ss}$ over all α' , then $\dot{p}_\alpha(t) \leq 0$ ($\dot{p}_\alpha(t) \geq 0$). This assertion implies the desired maximum (and corresponding minimum), thus concluding the proof. \square

Proposition 3.1 states that, relative to the steady state, the solution $p_\alpha(t)$ of (2.5) will never deviate more than the initial data. In other words, the system cannot be driven far away from the steady-state distribution.

Remark 3.2. If the initial data $p_\alpha(0)$ satisfies

$$(3.11) \qquad \max_{\alpha} \frac{p_\alpha(0)}{p_\alpha^{ss}} \leq C,$$

for a parameter-independent constant C , then Proposition 3.1 implies $p_\alpha(t) \lesssim p_\alpha^{ss}$ for all $t > 0$. This property will enable us to estimate certain averages in section 4.

Remark 3.3. In general, Proposition 3.1 cannot be applied to the full mass-dependent master equation (2.1) since the assumption of existence of a nontrivial steady state, and therefore (3.9), does not hold for (2.1) when $\epsilon > 0$. To see this, consider (2.1) after marginalizing in α . The resulting equation,

$$(3.12) \qquad \dot{p}_m(t) = F [p_{m-1}(t) - p_m(t)],$$

subject to $p_0(0) = 1$, is satisfied by the Poisson distribution $p_m(t) = \frac{(Ft)^m e^{-Ft}}{m!}$, for which $p_m(t) = 0$ for any $m = \mathcal{O}(1)$ in the limit as $t \rightarrow \infty$. Thus, no nontrivial steady state exists.

Remark 3.4. Proposition 3.1 and Remark 3.2 apply to the truncated master equation (3.3) *unconditionally* since a steady state is guaranteed to exist [12]. Note that the state space is finite-dimensional in this case.

4. Exact averaging: Discrete mesoscale model. In this section, we heuristically show how discrete variables that form averages of microscale quantities on the lattice are plausibly related to mesoscale observables of physical interest. In particular, diffusion equation (2.9) and step velocity law (2.8) have clear discrete counterparts. A noteworthy finding is a set of discrete boundary conditions at the step which only *partially* agrees with linear kinetic relation (2.11). In fact, our exact formulas for discrete fluxes at the left and right of the step edge manifest corrections to (2.11).

4.1. Definitions of basic averages. We now define the average step position, $\zeta(t)$, in terms of probabilities $p_{\alpha,m}(t)$.

DEFINITION 4.1 (average step position). *The average step position is*

$$(4.1) \quad \zeta(t) = a \sum_{\alpha,m} s(\alpha, m) p_{\alpha,m}(t),$$

where $s(\alpha, m)$, given in Definition 2.2, is an integer that denotes the site directly to the right of the step edge in the fixed reference frame of the 1D lattice.

Note that, in Definition 4.1, $|\alpha| - (m - m_0)$ is the number of adatoms that are exchanged with the step edge and, thus, solely contribute to step motion.

Next, we define the adatom number per lattice site, which plays the role of the adatom density in the mesoscale picture. We use the following two interrelated variables: (i) The density, $c_j(t)$, of adatoms *relative* to the step, where \hat{j} counts the lattice sites to the *right* of the step. This $c_j(t)$ is a Lagrangian variable. (ii) The Eulerian density, $\rho_j(t)$, at site j of the fixed 1D lattice.

DEFINITION 4.2 (Lagrangian and Eulerian adatom density). (i) *The Lagrangian-type adatom density is defined by*

$$(4.2a) \quad \begin{aligned} c_j(t) &= \sum_{\alpha,m} \nu_j(\alpha) p_{\alpha,m}(t) / a \\ &= \sum_{\alpha} \nu_j(\alpha) p_{\alpha}(t) / a, \end{aligned}$$

where $\nu_j(\alpha)$ is the number of adatoms at site \hat{j} for a system with adatom configuration α .

(ii) *The Eulerian adatom density is*

$$(4.2b) \quad \rho_j(t) = \sum_{\alpha,m} \nu_{j-s(\alpha,m)}(\alpha) p_{\alpha,m}(t) / a,$$

where $j - s(\alpha, m)$ is the Lagrangian coordinate corresponding to Eulerian j .

Regarding Definition 4.2, it is important to note that $\nu_j(\alpha)$ is a factor counting the number of instances of \hat{j} in multiset α . Since both \hat{j} and α use the same coordinate system, $\nu_j(\alpha)$ is independent of m , allowing for $c_j(t)$ to be expressed in terms of the marginal PDF $p_{\alpha}(t)$. In contrast, the definition of $\rho_j(t)$ cannot be written in terms of $p_{\alpha}(t)$ because of the mass dependence in the index of $\nu_{j-s(\alpha,m)}(\alpha)$.

The variable $c_j(t)$ is most useful in discrete equations for fluxes and boundary conditions at the step (section 4.2). On the other hand, $\rho_j(t)$ is more convenient to use in the derivation of the discrete diffusion equation, at lattice sites sufficiently away from the step edge (section 4.3).

Remark 4.3. For $F = 0$, the equilibrium adatom density, c^{eq} , at any lattice site can be computed by (3.2) and (4.2a) or, alternatively, directly from partition function (3.1) since the number of adatoms is constant everywhere on the terrace:

$$(4.3) \quad c^{eq} = \frac{\langle n \rangle}{(N-1)a} = \frac{k/a}{1-k},$$

where $\langle n \rangle$ denotes the average total number of adatoms.

We now proceed to define the adatom fluxes at the step edge by virtue of our rules for atomistic transitions (section 2.1.2).

DEFINITION 4.4 (adatom fluxes at step). *The flux J_{\pm} on the right (+, lower terrace) or left (-, upper terrace) of the step edge is*

$$(4.4) \quad J_{\pm}(t) = \pm \sum_{\alpha, m} \mathbb{1}(\nu_{-1}(\alpha) = 0) \times [T_{(\alpha_{\pm}, m), (\alpha, m)} p_{\alpha, m}(t) - T_{(\alpha, m), (\alpha_{\pm}, m)} p_{\alpha_{\pm}, m}(t)].$$

Here, the indicator function $\mathbb{1}(\cdot)$ equals 1 if its argument is true and 0 otherwise, and $\alpha_{\pm} = \tilde{\alpha} \cup \{\pm 1\}$ denotes the adatom configuration resulting from a rightward (+) or leftward (-) detachment. The factor $\mathbb{1}(\nu_{-1}(\alpha) = 0)$ excludes configurations that involve adatoms on top of the edge atom, i.e., those configurations for which detachment is forbidden and which are inaccessible via attachment events. Additionally, the external deposition of adatoms does not contribute to the mass flux J_{\pm} , and therefore only a single value of m enters (4.4); see (2.3).

4.2. Generalized discrete flux at step edge. In this section, we derive an exact expression for the discrete flux at the step edge. This expression forms the basis for characterizing *corrections* to linear kinetic law (2.11) in the discrete setting.

By manipulating (4.4), we directly find a formula for the flux in terms of atomistic parameters, the differences $c_{\pm 1}(t) - c^{eq}$, and other discrete averages, viz.,

$$(4.5) \quad \begin{aligned} J_+(t) &= \sum_{\alpha, m} \mathbb{1}(\nu_{-1}(\alpha) = 0) [T_{(\alpha_+, m), (\alpha, m)} p_{\alpha, m}(t) - T_{(\alpha, m), (\alpha_+, m)} p_{\alpha_+, m}(t)] \\ &= Dk\phi_+ \sum_{\alpha, m} \mathbb{1}(\nu_{-1}(\alpha) = 0) p_{\alpha, m}(t) - D\phi_+ \sum_{\alpha, m} \mathbb{1}(\nu_1(\alpha) = 1) p_{\alpha, m}(t) \\ &= Dk\phi_+ \sum_{\alpha} \mathbb{1}(\nu_{-1}(\alpha) = 0) p_{\alpha}(t) - D\phi_+ \sum_{\alpha} \mathbb{1}(\nu_1(\alpha) = 1) p_{\alpha}(t) \\ &= Dk\phi_+ \left[1 - \sum_{\alpha} \mathbb{1}(\nu_{-1}(\alpha) > 0) p_{\alpha}(t) \right] \\ &\quad - D\phi_+ \sum_{\alpha} \mathbb{1}(\nu_1(\alpha) = 1) \nu_1(\alpha) p_{\alpha}(t) \\ &= D\phi_+ a \left[\frac{k/a}{1-k} (1-k) - k \sum_{\alpha} \mathbb{1}(\nu_{-1}(\alpha) > 0) p_{\alpha}(t)/a \right] \\ &\quad - D\phi_+ a \left[c_1(t) - \sum_{\alpha} \mathbb{1}(\nu_1(\alpha) > 1) \nu_1(\alpha) p_{\alpha}(t)/a \right] \\ &= -D\phi_+ a [c_1(t) - c^{eq}] - D\phi_+ a f_+(t). \end{aligned}$$

In the above, the second equality results from substitution of the transition rates (2.2); the third equality results from summing over the mass variable; the fourth equality makes use of the complement rule, $\mathbb{1}(\nu_{-1}(\alpha) = 0) = 1 - \mathbb{1}(\nu_{-1}(\alpha) > 0)$; and the fifth equality involves adding and subtracting the last sum to make $c_1(t)$ appear. Similar steps can be used to derive the corresponding formula for $J_-(t)$. Together, these fluxes can be written as

$$(4.6) \quad J_{\pm}(t) = \mp D\phi_{\pm} a [c_{\pm 1}(t) - c^{eq}] \mp D\phi_{\pm} a f_{\pm}(t).$$

In (4.6), the first term on the right-hand side is the discrete analogue of the linear kinetic relation of the BCF model. We invoke the definitions for $c_{\pm 1}(t)$ and c^{eq} according to (4.2a) and (4.3), respectively, and define

$$(4.7a) \quad \begin{aligned} f_+(t) = k & \left[c^{eq} + \sum_{\alpha} \mathbb{1}(\nu_{-1}(\alpha) > 0) p_{\alpha}(t)/a \right] \\ & - \sum_{\alpha} \mathbb{1}(\nu_1(\alpha) > 1) \nu_1(\alpha) p_{\alpha}(t)/a \end{aligned}$$

and

$$(4.7b) \quad \begin{aligned} f_-(t) = k & \left[c^{eq} + \sum_{\alpha} \mathbb{1}(\nu_{-1}(\alpha) > 0) p_{\alpha}(t)/a \right] \\ & - \sum_{\alpha} \mathbb{1}(\nu_1(\alpha) > 0) \nu_{-1}(\alpha) p_{\alpha}(t)/a \\ & - \sum_{\alpha} \mathbb{1}(\nu_1(\alpha) = 0) \mathbb{1}(\nu_{-1}(\alpha) > 1) \\ & \quad \times [\nu_{-1}(\alpha) - 1] p_{\alpha}(t)/a. \end{aligned}$$

Equations (4.7) signify corrections to the discrete analogue of the linear kinetic law of the BCF model; cf. (2.11) and (4.6). The corresponding *corrective* fluxes, f_{\pm} , measure the frequency by which the atomistic system visits configurations that forbid detachment of the edge atom or attachment of an adatom from the right (+) or left (−) of the step edge. We expect that the magnitudes of correction terms f_{\pm} are negligibly small in the appropriate low-density regime for adatoms [19, 20].

In section 5, we find bounds for the above corrective fluxes, f_{\pm} . In particular, we systematically describe a parameter regime for k and F in which these corrections are negligible. In contrast, if $f_{\pm}(t)$ are important, then the discrete fluxes $J_{\pm}(t)$ may no longer have a linear dependence on $c_{\pm 1}(t)$, which in turn signifies the onset of high-supersaturation behavior; see section 6.

4.3. Discrete diffusion and step velocity law. In this section, we formally describe the change of the adatom density and average step position with time. In addition, we complement (4.6) with a mass-transport relation between discrete fluxes and densities near the step edge, which forms a discrete analogue of Fick's law for diffusion. What we find are equations for discrete diffusion and discrete versions of Fick's law that have correction terms resulting from atomistic configurations with multiple adatoms at the same lattice site.

First, by Definition 4.2 and master equation (2.1), the time evolution of $\rho_j(t)$ is described by

$$(4.8) \quad \begin{aligned} \dot{\rho}_j(t) &= \sum_{\alpha, m} \nu_{j-s(\alpha, m)}(\alpha) \sum_{\substack{(\alpha', m') \\ \neq (\alpha, m)}} [T_{(\alpha, m), (\alpha', m')} p_{\alpha', m'}(t) - T_{(\alpha', m'), (\alpha, m)} p_{\alpha, m}(t)] / a \\ &= \sum_{\alpha, m} \sum_{\alpha', m'} [\nu_{j-s(\alpha, m)}(\alpha) - \nu_{j-s(\alpha', m')}(\alpha')] T_{(\alpha, m), (\alpha', m')} p_{\alpha', m'}(t) / a. \end{aligned}$$

In (4.8) we invoke (2.2e) for the transition rates to make the difference $\nu_{j-s(\alpha, m)}(\alpha) - \nu_{j-s(\alpha', m')}(\alpha')$ appear. By identifying values of this difference, most of which are zero, it is possible to simplify our formula for $\dot{\rho}_j(t)$ and express the right-hand side of (4.8) in terms of known averages.

Remark 4.5. It should be noted that the derivation of (4.8) is independent of our definition of $\nu_j(\alpha)$. Equations similar to (4.8) can be found by using a general property of master equations for Markov processes, namely, the property that transitions must conserve probability. In particular, the above also applies if $\nu_j(\alpha)$ is replaced with $\mathbb{1}(\nu_j(\alpha) > 0)$, which amounts to using the definition of adatom density in [20].

Now, by transition rates (2.2) and our definition of $\nu_j(\alpha)$, we write (4.8) as [25]

$$\begin{aligned}
 \dot{\rho}_j(t) &= D [\rho_{j-1}(t) - 2\rho_j(t) + \rho_{j+1}(t)] + \frac{F}{(N-1)a} \\
 &\quad - D [R_{j-1}(t) - 2R_j(t) + R_{j+1}(t)] \\
 &\quad - \sum_{\alpha,m} \left\{ \delta_{j,s(\alpha,m)} \left[D\mathbb{1}(\nu_{-1}(\alpha) > 0) + D\mathbb{1}(\nu_1(\alpha) > 0) + \frac{F}{N-1} \right] \right. \\
 &\quad \quad - \delta_{j,s(\alpha,m)-1} \left[D\mathbb{1}(\nu_{-1}(\alpha) > 0) + Dk\phi_- \mathbb{1}(\nu_{-1}(\alpha) = 0) \right. \\
 &\quad \quad \quad \left. \left. - D\phi_- \mathbb{1}(\nu_1(\alpha) = 0)\mathbb{1}(\nu_{-1}(\alpha) > 0) \right] \right. \\
 &\quad \quad \left. - \delta_{j,s(\alpha,m)+1} \left[D\mathbb{1}(\nu_1(\alpha) > 0) + Dk\phi_+ \mathbb{1}(\nu_{-1}(\alpha) = 0) \right. \right. \\
 &\quad \quad \quad \left. \left. - D\phi_+ \mathbb{1}(\nu_1(\alpha) = 1) \right] \right\} p_{\alpha,m}(t)/a.
 \end{aligned}
 \tag{4.9}$$

A few comments on (4.9) are in order. The first two lines include a diffusion-type second-order difference scheme for $\rho_j(t)$ and the accompanying correction to discrete diffusion, respectively. The third line of (4.9) removes certain terms that do not contribute when $j = s(\alpha, m)$; no atoms are deposited to the step edge, for example. The remaining terms express boundary conditions at the right ($j = s(\alpha, m) + 1$) or left ($j = s(\alpha, m) - 1$) of the step; they contribute only when j is in the vicinity of the step via the Kronecker delta functions. The high-occupation correction terms, $R_j(t)$, are defined as

$$R_j(t) = \sum_{\alpha,m} [\nu_{j-s(\alpha,m)}(\alpha) - \mathbb{1}(\nu_{j-s(\alpha,m)}(\alpha) > 0)] p_{\alpha,m}(t)/a.
 \tag{4.10}$$

Equation (4.10) measures discrete corrections related to certain correlated motion of adatoms. In particular, these corrections to discrete diffusion arise from the fact that the KRSOS model includes constant adatom hopping rates, regardless of the number of adatoms present at a given lattice site. In effect, atomistic configurations with multiple adatoms at the same lattice site introduce interactions between particles since only one atom is able to move. This high-occupancy effect is seen in (4.10) since $\nu_{j-s(\alpha,m)}(\alpha) - \mathbb{1}(\nu_{j-s(\alpha,m)}(\alpha) > 0) \neq 0$ when two or more adatoms are at site j .

The fourth and fifth lines of (4.9) suggest that

$$\begin{aligned}
 &D \sum_{\alpha,m} \left[\mathbb{1}(\nu_{-2}(\alpha) > 0) - \mathbb{1}(\nu_{-1}(\alpha) > 0) + k\phi_- \mathbb{1}(\nu_{-1}(\alpha) = 0) \right. \\
 &\quad \left. - \phi_- \mathbb{1}(\nu_1(\alpha) = 0)\mathbb{1}(\nu_{-1}(\alpha) > 0) \right] p_{\alpha,m}(t)/a \\
 &= D [c_{-2}(t) - c_{-1}(t)] - a^{-1}J_-(t) - D [\hat{R}_{-2}(t) - \hat{R}_{-1}(t)],
 \end{aligned}
 \tag{4.11a}$$

where J_- is defined by (4.4). The analogous result can be reached for the last two

lines of (4.9), yielding the corresponding condition for J_+ , at the left of the step edge:

$$(4.11b) \quad \begin{aligned} & D \sum_{\alpha, m} \left[\mathbb{1}(\nu_2(\alpha) > 0) - \mathbb{1}(\nu_1(\alpha) > 0) + k\phi_+ \mathbb{1}(\nu_{-1}(\alpha) = 0) \right. \\ & \quad \left. - \phi_+ \mathbb{1}(\nu_1(\alpha) = 1) \right] p_{\alpha, m}(t)/a \\ & = D [c_2(t) - c_1(t)] + a^{-1} J_+(t) - D [\hat{R}_2(t) - \hat{R}_1(t)]. \end{aligned}$$

It should be noted that the high-occupation terms $\hat{R}_j(t)$ found in (4.11) are corrections of the same origin as (4.10), but represented in Lagrangian coordinates. These are

$$(4.12) \quad \hat{R}_j(t) = \sum_{\alpha} [\nu_j(\alpha) - \mathbb{1}(\nu_j(\alpha) > 0)] p_{\alpha}(t)/a.$$

In view of (4.11), we can now extract the discrete boundary terms at the step edge by setting $j = s(\alpha, m) \pm 1$ ($j = \pm 1$) in (4.9). Hence, we find

$$(4.13) \quad J_{\pm}(t) = \mp Da [c_{\pm 2}(t) - c_{\pm 1}(t)] \mp Da [\hat{R}_{\pm 2}(t) - \hat{R}_{\pm 1}(t)].$$

Equations (4.13) are a semidiscrete version of Fick's law including corrections to diffusive fluxes at each side of the step edge.

Remark 4.6. In contrast to (2.10), the advection term *at the step edge* does not appear in (4.13). We have not been able to derive this term from the atomistic model. We attribute this inability to the fact that certain atomistic processes at the step edge are forbidden; see (2.3a) and (2.3b). In effect, these forbidden processes can cause adatoms to pile up in front of the step edge, thereby conserving mass at that atomistic scale.

We now provide the anticipated mass conservation statement that involves the average step velocity, $\zeta(t)$; see Definition 4.1. This average is explicitly expressed by use of master equation (2.1), ensemble average (4.1) for $\zeta(t)$, and formula (4.4) for fluxes J_{\pm} . It can be shown that [25]

$$(4.14) \quad \zeta(t) = a [J_-(t) - J_+(t)].$$

We omit the details for the derivation of this result.

In summary, motion laws (4.9) and (4.14) form discrete analogues to BCF-type equations (2.8)–(2.10), notwithstanding advection. The correction terms $R_j(t)$ and $\hat{R}_j(t)$, respectively appearing in (4.9) and (4.11b), are negligible if the system parameters are suitably scaled with the lattice spacing, a [20]. A systematic, formal analysis of these corrections is given in section 5.

5. Estimates for discrete corrections and emergence of continuum step flow. In this section, we systematically derive ℓ^∞ -bounds for the discrete corrections of section 4 via Proposition 3.1, in order to illuminate the behavior of these corrections with the kinetic parameters k and F when $\epsilon = F/D$ is sufficiently small (section 5.1). For the sake of completeness, we also extract the continuum step-flow equations of the discrete mesoscale model in the limit where the lateral lattice spacing, a , approaches zero, and the microscale kinetic parameters scale properly with a (section 5.2). Our estimates apply to (i) the correction terms $f_{\pm}(t)$ found in fluxes (4.6), and (ii) high-occupation corrections to discrete density, e.g., the terms $\hat{R}_j(t)$, described in section 4.3.

Our formal argument forms an extension of the deposition-free (with $F = 0$) case [20] under the hypothesis that only a finite number of particle states contribute to system evolution; $|\alpha| \leq M$ (see section 3.2). Consequently, as $a \downarrow 0$ we extract error estimates for the emerging diffusion equation and the linear kinetic law at the step edge.

5.1. Bounds for discrete corrections. The first part of our program can be outlined as follows. First, in view of Remark 3.2 for the initial data $p_\alpha(0)$, we estimate $f_\pm(t)$ and $\hat{R}_j(t)$ in terms of the marginal steady-state solution $p_\alpha^{ss,\epsilon}$ of the master equation. Second, by invoking the ϵ -series expansion of section 3.2 for $p_\alpha^{ss,\epsilon}$, we derive the desired estimates for $f_\pm(t)$ and $\hat{R}_j(t)$ if ϵ is small enough; these signify corrections to the linear kinetic law for the adatom fluxes, J_\pm , and high-occupation corrections to the discrete diffusion equation on the terrace, respectively. This second stage of our derivation of bounds on discrete corrections makes use of the equilibrium distribution p_α^{eq} , equation (3.2), for ϵ^0 -terms in our formal expansion, and the ϵ^1 -terms found in (3.7). In principle, higher-order terms can also be computed but are neglected in our analysis.

PROPOSITION 5.1. *The corrective fluxes (4.7) at the step edge satisfy the estimate*

$$(5.1) \quad f_\pm(t) = \mathcal{O}\left(\frac{k}{1-k} \frac{k}{a}, \frac{\epsilon N}{(1+\phi)a}\right),$$

where $\phi = \phi_+$ or ϕ_- . Similarly, the high-occupation corrections (4.12) to densities satisfy

$$(5.2) \quad \hat{R}_j(t) = \mathcal{O}\left(\frac{k}{1-k} \frac{k}{a}, \frac{\epsilon N}{a}\right).$$

In these estimates, the constants entering the respective bounds are independent of time and parameters of the problem.

Thus, by Proposition 5.1, if we assume that $k/a = \mathcal{O}(1)$, $\phi \leq \mathcal{O}(1)$ [20, 14], and $\epsilon < \mathcal{O}(a^2)$, we can assert that $f_\pm(t)$ can be neglected when compared to the linear-in-density part of the discrete flux $J_\pm(t)$. Furthermore, the corrections $\hat{R}_j(t)$ are small compared to density $c_j(t)$, and therefore $R_j(t) \ll \rho_j(t)$ as well. These controlled approximations reveal a kinetic regime in which (4.6), (4.13), and the discrete diffusion equation in (4.9) reduce to discrete versions of linear kinetic law (2.11), Fick’s law (2.10), and the continuum diffusion equation for density.

The remainder of this subsection is devoted to heuristically proving Proposition 5.1. We will invoke (4.7) and (4.12) for $f_\pm(t)$ and $\hat{R}_j(t)$; in these sums, there are no mass- (m -) dependent terms since these have already been summed out.

Proof. We proceed to derive (5.1) and (5.2) through heuristics. Define

$$(5.3a) \quad \begin{aligned} \tilde{f}_+^{ss,\epsilon} &:= k \left[c^{eq} + \sum_{\alpha} \mathbb{1}(\nu_{-1}(\alpha) > 0) p_{\alpha}^{ss,\epsilon} / a \right] \\ &+ \sum_{\alpha} \mathbb{1}(\nu_1(\alpha) > 1) \nu_1(\alpha) p_{\alpha}^{ss,\epsilon} / a, \end{aligned}$$

$$(5.3b) \quad \begin{aligned} \tilde{f}_-^{ss,\epsilon} &:= k \left[c^{eq} + \sum_{\alpha} \mathbb{1}(\nu_{-1}(\alpha) > 0) p_{\alpha}^{ss,\epsilon} / a \right] \\ &+ \sum_{\alpha} \mathbb{1}(\nu_1(\alpha) > 0) \nu_{-1}(\alpha) p_{\alpha}^{ss,\epsilon} / a \\ &+ \sum_{\alpha} \mathbb{1}(\nu_1(\alpha) = 0) \mathbb{1}(\nu_{-1}(\alpha) > 1) [\nu_{-1}(\alpha) - 1] p_{\alpha}^{ss,\epsilon} / a, \text{ and} \end{aligned}$$

$$(5.3c) \quad \hat{R}_j^{ss,\epsilon} := \sum_{\alpha} [\nu_j(\alpha) - \mathbb{1}(\nu_j(\alpha) > 0)] p_{\alpha}^{ss,\epsilon} / a.$$

By Remark 3.2 and exact formulas (4.7) and (4.12) for $f_{\pm}(t)$ and $\hat{R}_j(t)$, respectively, we have

$$(5.4) \quad |f_{\pm}(t)| \lesssim \tilde{f}_{\pm}^{ss,\epsilon}, \text{ and } |\hat{R}_j(t)| \lesssim \hat{R}_j^{ss,\epsilon}, \quad t > 0.$$

Inequalities (5.4) are not particularly useful since they do not explicitly manifest the dependence on the kinetic parameters of interest. We need to use some results from section 3.2 in order to refine these estimates.

In correspondence to (3.7) for the truncated system, we write $p_{\alpha}^{ss,\epsilon} = p_{\alpha}^{ss,(0)} + \epsilon p_{\alpha}^{ss,(1)} + \mathcal{O}(\epsilon^2)$, where $p_{\alpha}^{ss,(l)}$ is the l th order term of the underlying series expansion in $\epsilon = F/D$; in particular, $p_{\alpha}^{ss,(0)} = p_{\alpha}^{eq}$ is the zeroth-order contribution to the steady state. The constant entering the term $\mathcal{O}(\epsilon^2)$ may depend on parameters of the problem but is immaterial for our purposes. We will neglect terms with $l \geq 2$ in the ϵ -expansion for $p_{\alpha}^{ss,\epsilon}$.

By inspection of (5.3), we define the following sums:

$$(5.5a) \quad S_1^{(l)} := \sum_{\alpha} \mathbb{1}(\nu_{-1}(\alpha) > 0) p_{\alpha}^{ss,(l)},$$

$$(5.5b) \quad S_2^{(l)} := \sum_{\alpha} \mathbb{1}(\nu_1(\alpha) > 1) \nu_1(\alpha) p_{\alpha}^{ss,(l)},$$

$$(5.5c) \quad S_3^{(l)} := \sum_{\alpha} \mathbb{1}(\nu_1(\alpha) > 0) \nu_{-1}(\alpha) p_{\alpha}^{ss,(l)},$$

$$(5.5d) \quad S_4^{(l)} := \sum_{\alpha} \mathbb{1}(\nu_1(\alpha) = 0) \mathbb{1}(\nu_{-1}(\alpha) > 1) [\nu_{-1}(\alpha) - 1] p_{\alpha}^{ss,(l)},$$

$$(5.5e) \quad S_5^{(l)} := \sum_{\alpha} [\nu_j(\alpha) - \mathbb{1}(\nu_j(\alpha) > 0)] p_{\alpha}^{ss,(l)}.$$

Accordingly, formulas (5.3) are recast into the forms

$$(5.6a) \quad \tilde{f}_+^{ss,\epsilon} = kc^{eq} + \frac{k}{a} [S_1^{(0)} + \epsilon S_1^{(1)}] + \frac{1}{a} [S_2^{(0)} + \epsilon S_2^{(1)}] + \mathcal{O}(\epsilon^2),$$

$$(5.6b) \quad \begin{aligned} \tilde{f}_-^{ss,\epsilon} &= kc^{eq} + \frac{k}{a} [S_1^{(0)} + \epsilon S_1^{(1)}] + \frac{1}{a} [S_3^{(0)} + \epsilon S_3^{(1)}] \\ &\quad + \frac{1}{a} [S_4^{(0)} + \epsilon S_4^{(1)}] + \mathcal{O}(\epsilon^2), \end{aligned}$$

$$(5.6c) \quad \hat{R}_j^{ss,\epsilon} = \frac{1}{a} [S_5^{(0)} + \epsilon S_5^{(1)}] + \mathcal{O}(\epsilon^2).$$

First, we compute $S_i^{(0)}$ ($i = 1, 2, 3, 4, 5$), which amount to contributions from the equilibrium solution of the master equation, for $F = 0$. By (3.2) and $0 < k < 1$, we write

$$(5.7) \quad \begin{aligned} S_1^{(0)} &= \frac{1}{Z} \sum_{\alpha} \mathbb{1}(\nu_{-1}(\alpha) > 0) k^{|\alpha|} \\ &= \frac{1}{Z} \sum_{n=1}^{\infty} \binom{n+N-3}{n-1} k^n = k. \end{aligned}$$

The binomial coefficient in (5.7) is the number of n -particle configurations with at least one adatom in the site immediately to the left of the step. Similarly, we have

$$(5.8) \quad \begin{aligned} S_2^{(0)} &= \frac{1}{Z} \sum_{\alpha} \mathbb{1}(\nu_1(\alpha) > 1) \nu_1(\alpha) k^{|\alpha|} \\ &= \frac{1}{Z} \sum_{r=2}^{\infty} r k^r \sum_{n=r}^{\infty} \binom{n-r+N-3}{n-r} k^{n-r} \\ &= (1-k) \sum_{r=2}^{\infty} r k^r = \frac{2k^2 - k^3}{1-k}, \end{aligned}$$

$$(5.9) \quad \begin{aligned} S_3^{(0)} &= \frac{1}{Z} \sum_{\alpha} \mathbb{1}(\nu_1(\alpha) > 0) \nu_{-1}(\alpha) k^{|\alpha|} \\ &= \frac{k}{Z} \sum_{r=1}^{\infty} r k^r \sum_{n=r+1}^{\infty} \binom{n-r-1+N-3}{n-r-1} k^{n-r-1} \\ &= k(1-k) \sum_{r=1}^{\infty} r k^r = \frac{k^2}{1-k}, \end{aligned}$$

$$(5.10) \quad \begin{aligned} S_4^{(0)} &= \frac{1}{Z} \sum_{\alpha} \mathbb{1}(\nu_1(\alpha) = 0) \mathbb{1}(\nu_{-1}(\alpha) > 1) [\nu_{-1}(\alpha) - 1] k^{|\alpha|} \\ &= \frac{k}{Z} \sum_{r=2}^{\infty} (r-1) k^{r-1} \sum_{n=r}^{\infty} \binom{n-r+N-4}{n-r} k^{n-r} \\ &= k(1-k)^2 \sum_{r=1}^{\infty} r k^r = k^2, \end{aligned}$$

and

$$\begin{aligned}
 S_5^{(0)} &= \frac{1}{Z} \sum_{\boldsymbol{\alpha}} [\nu_j(\boldsymbol{\alpha}) - \mathbb{1}(\nu_j(\boldsymbol{\alpha}) > 0)] k^{|\boldsymbol{\alpha}|} \\
 &= \frac{1}{Z} \sum_{r=2}^{\infty} (r-1) k^r \sum_{n=r}^{\infty} \binom{n-r+N-3}{n-r} k^{n-r} \\
 (5.11) \quad &= k(1-k) \sum_{r=1}^{\infty} r k^r = \frac{k^2}{1-k}.
 \end{aligned}$$

We have followed the convention that the index r is used to account for restrictions on states coming from indicator functions and the index n replaces the number of adatoms, $|\boldsymbol{\alpha}|$.

All that remains is to compute terms proportional to ϵ . This task calls for estimating the sums $S_i^{(l)}$, defined in (5.5), for $l = 1$. Hence, we would need to invoke the first-order steady-state solution, $p_{\boldsymbol{\alpha}}^{ss,(1)}$, of marginalized master equation (2.5). As alluded to in section 3.2, we do not have, strictly speaking, a simple closed-form solution. Instead, by restricting our attention to a finite number of particle states ($|\boldsymbol{\alpha}| \leq M$), we provide approximations for the requisite (infinite) sums by finite sums via expansion (3.7). This approximation amounts to replacing the sums $S_i^{(1)}$ with quadratic forms of appropriately defined vectors, $\mathbf{y}_i \in \mathbb{R}^{\Omega(M)}$; thus, we write $S_i^{(1)} \approx \mathbf{y}_i^T \mathfrak{A}^\dagger \mathbf{z}$, where the vectors \mathbf{y}_i have entries that correspond to the indicator functions and/or $\nu_{\pm 1}(\boldsymbol{\alpha})$ according to (5.5) and $\mathbf{z} = -\mathfrak{B} \mathbf{p}^0$.

Next, we obtain estimates for $S_i^{(1)}$ as follows (see section 3.2):

$$\begin{aligned}
 |S_i^{(1)}| &\approx |\mathbf{y}_i^T \mathfrak{A}^\dagger \mathbf{z}| \\
 &= \left| \left[\left(\frac{\mathbf{y}_i^T}{\mathbf{y}_i^T \mathbf{y}_i} \right)^T \right]^\dagger \mathfrak{A}^\dagger \left[\frac{\mathbf{z}^T}{\mathbf{z}^T \mathbf{z}} \right]^\dagger \right| \\
 &= \left[\frac{|\mathbf{z}^T \mathfrak{A} \mathbf{y}_i|}{\mathbf{y}_i^T \mathbf{y}_i \mathbf{z}^T \mathbf{z}} \right]^\dagger = \frac{\mathbf{y}_i^T \mathbf{y}_i \mathbf{z}^T \mathbf{z}}{|\mathbf{z}^T \mathfrak{A} \mathbf{y}_i|} \\
 (5.12) \quad &\lesssim |\mathbf{z}^T \mathfrak{A} \mathbf{y}_i|^{-1}
 \end{aligned}$$

if $\mathbf{z}^T \mathfrak{A} \mathbf{y}_i \neq 0$. The above calculation uses several properties of the Moore–Penrose pseudoinverse; i.e., $\mathbf{y}^\dagger = \mathbf{y}^T / (\mathbf{y}^T \mathbf{y})$ provided $\mathbf{y} \neq \mathbf{0}$ (second line), $(\mathfrak{A} \mathfrak{B})^\dagger = \mathfrak{B}^\dagger \mathfrak{A}^\dagger$ (third line), and the pseudoinverse of a nonzero constant is its multiplicative inverse (fourth line). The last line of (5.12) results from observing that the numerator results in a fixed constant for each i . Since \mathfrak{A} , \mathfrak{B} , \mathbf{p}^0 , and \mathbf{y}_i are known, (5.12) is a computable estimate. After some linear algebra, we find

$$(5.13) \quad |S_i^{(1)}| \lesssim \begin{cases} \frac{N}{1+\phi}, & i = 1, 2, 3, 4, \\ N, & i = 5; \end{cases}$$

in the above, $\phi = \phi_+$ or ϕ_- .

In summary, if the initial data of the atomistic system is near the steady state in the sense of (3.11), then Proposition 3.1 implies (5.4). Inequalities (5.4) along with (5.5)–(5.13) yield estimates (5.1) and (5.2) for sufficiently small ϵ and k . This statement concludes our proof of Proposition 5.1. \square

Remark 5.2. The estimates in Proposition 5.1 are based upon several assumptions and approximations, including: (i) application of Proposition 3.1; (ii) replacement of marginalized master equation (2.5) by a matrix equation if $|\alpha| \leq M$; (iii) truncation of a formal power-series expansion for the steady-state distribution, p_{α}^{ss} ; and (iv) ℓ^{∞} -bounds for correction terms (4.7) and (4.12). Consequently, estimates (5.1) and (5.2) are not expected to be optimal. In particular, the bounds involving ϵ can likely be improved.

5.2. BCF-type model as a scaling limit. Proposition 5.1 enables us to systematically extract the scaling limit of the atomistic model, which leads to the verification of major ingredients of the BCF-type description of section 2.2. The derivation of the scaling limit on the basis of error estimates here aims to shed some light on the kinetic regime in which the BCF model is valid in the presence of growth ($F \neq 0$).

In view of (5.2), let us impose

$$(5.14) \quad k = \mathcal{O}(a), \quad \epsilon = \mathcal{O}(a^3),$$

which ensure that high-occupancy corrections $\hat{R}_j(t)$ and $R_j(t)$ are small compared to the corresponding densities. On the other hand, we assume $\rho_j(t) \rightarrow \rho(x, t)$ and $c_j(t) \rightarrow \mathcal{C}(\hat{x}, t)$ as the lattice parameter approaches zero, $a \rightarrow 0$. The Taylor expansion of $\rho(x, t)$ about $x = ja$ yields

$$\frac{\rho_{j-1}(t) - 2\rho_j(t) + \rho_{j+1}(t)}{a^2} = \frac{\partial^2 \rho}{\partial x^2}(ja, t) + \mathcal{O}(a^2).$$

By the usual notion of macroscopic diffusion, it is natural to set $\mathcal{D} := Da^2 = \mathcal{O}(1)$, the surface diffusivity, and $\mathcal{F} := \frac{F}{(N-1)a}$, the deposition flux per unit length [20, 14]. Thus, the first two lines of (4.9), with (5.14), imply

$$(5.15) \quad \frac{\partial \rho}{\partial t} = \mathcal{D} \frac{\partial^2 \rho}{\partial x^2} - \mathcal{D} \frac{\partial^2 \mathcal{R}}{\partial x^2} + \mathcal{F},$$

as $a \rightarrow 0$, where $\mathcal{R}(x, t)$ is the continuum limit of $R_j(t)$. By (5.14), the terms $\mathcal{D} \partial^2 \mathcal{R} / \partial x^2$ and \mathcal{F} are $\mathcal{O}(a)$, and hence are negligible to leading order. With the exception of the deposition term, the resulting leading-order equation for $\rho(x, t)$ is the anticipated diffusion equation in Eulerian coordinates; cf. (2.9). By sharpening estimates for ϵ in Proposition 5.1, \mathcal{F} may subsequently appear as a leading-order term.

Furthermore, the observation that $\hat{R}_j(t) = \mathcal{O}(a)$ enables us to obtain Fick's law of diffusion at the step edge by virtue of (4.13). By Taylor expanding the Lagrangian adatom density, \mathcal{C} , about $\hat{x} = \hat{j}a$ with $\hat{j} = 0$ for the right (+) side of the step and $\hat{j} = N - 1$ for the left (-) side of the step as $a \rightarrow 0$, we obtain the formulas

$$(5.16a) \quad J_+(t) = -\mathcal{D} \left. \frac{\partial \mathcal{C}}{\partial \hat{x}} \right|_{\hat{x}=0^+} + \mathcal{O}(a),$$

$$(5.16b) \quad J_-(t) = -\mathcal{D} \left. \frac{\partial \mathcal{C}}{\partial \hat{x}} \right|_{\hat{x}=L^-} + \mathcal{O}(a),$$

where $\hat{x} = \hat{j}a$ and $L = Na = \mathcal{O}(1)$ by virtue of the screw-periodic boundary conditions. In the above, we used the expansions $c_2(t) - c_1(t) = a[(\partial \mathcal{C} / \partial \hat{x})|_{x=0^+} + \mathcal{O}(a)]$ and $c_{-2}(t) - c_{-1}(t) = a[-(\partial \mathcal{C} / \partial \hat{x})|_{x=L^-} + \mathcal{O}(a)]$.

Equations (5.16) need to be complemented with kinetic boundary conditions at the step edge. Hence, we now apply (4.6) with (4.7) and (5.1). First, we set $\kappa_{\pm} :=$

$D\phi_{\pm}a = \mathcal{O}(1)$ [20, 14]. Second, by inspection of estimate (5.1), we assume $\phi_{\pm} \leq \mathcal{O}(1)$ along with (5.14). Consequently, we can assert that $|f_{\pm}(t)| = \mathcal{O}(a)$. Thus, by (4.6) we obtain

$$(5.17a) \quad J_+(t) = -\kappa_+ [\mathcal{C}(0^+, t) - c^{eq}] + \mathcal{O}(a),$$

$$(5.17b) \quad J_-(t) = \kappa_- [\mathcal{C}(L^-, t) - c^{eq}] + \mathcal{O}(a)$$

as $a \rightarrow 0$; recall that $c^{eq} = (k/a)(1-k)^{-1} \approx k/a$ if $k = \mathcal{O}(a)$ [20].

The last component of the BCF model that emerges from the discrete equations is the step velocity law. This law is provided by (4.14); in this equation, the factor multiplying the difference in the adatom flux across the step edge equals Ω/a' . Thus, (4.14) is precisely (2.8) pertaining to the BCF model.

6. Corrections to BCF-type linear kinetic relation: A numerical study.

In this section, we carry out KMC simulations to illustrate the behavior of adatom fluxes at the step edge for high enough supersaturations, defined as $\sigma_{\pm} = c_{\pm 1}/c^{eq} - 1$. We demonstrate that in this regime of high detachment or deposition flux, described in more detail below, the boundary condition for the adatom fluxes at the step edge can deviate significantly from linear kinetic relation (5.17); thus, in principle the corrective fluxes, $f_{\pm}(t)$, may *not* be negligible. Since we have been unable to express these contributions, f_{\pm} , in terms of mesoscale quantities such as the adatom density, KMC simulations remain our primary tool for describing the high-supersaturation effects. For a discussion of this point, see section 7.

First, we make an educated (yet empirical) attempt to outline plausible conditions by which the conventional BCF model, particularly the linear kinetic relation for the flux, becomes questionable. By estimate (5.1) of Proposition 5.1, the microscale system may no longer be modeled in accordance with the BCF theory if, for example, $k = \mathcal{O}(1)$, or $k = \mathcal{O}(a)$ and $\epsilon = \mathcal{O}(a)$. These conditions indicate situations in which high supersaturation may occur because of a large enough detachment rate at the step edge or high enough deposition onto the surface from above.

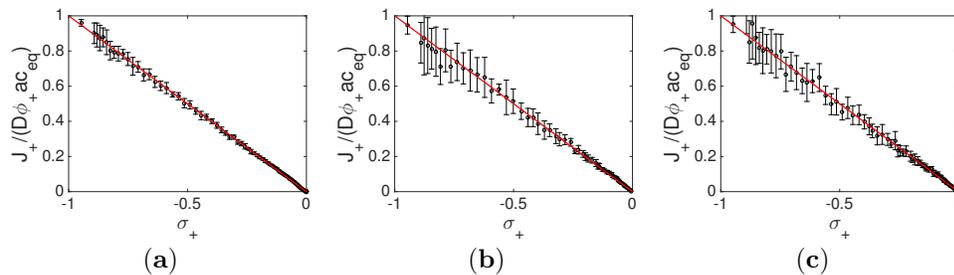


FIG. 4. (Color available online.) Plots of KMC simulations (circles) and the linear kinetic law (red solid line) for adatom flux versus supersaturation on the right of step edge for different values of deposition rate, F , with $N = 50$, $D = 10^{10}$, $k \approx 0.0025$, and $\phi_{\pm} = 1$. From left to right: (a) $F = 0$ ($\epsilon = 0$); (b) $F = 10^6$ ($\epsilon = 10^{-4}$); and (c) $F = 10^7$ ($\epsilon = 10^{-3}$). In each plot, the solid line represents linear kinetic law (5.17), by neglect of f_{\pm} . The error bars are determined by use of the standard deviation of flux in (a) 10 ensembles of 10^7 simulations; and (b), (c) 10 ensembles of 10^6 simulations. Evidently, on average the system evolves close to thermodynamic equilibrium, in accordance with the BCF model.

Figure 4 depicts the adatom flux on the right of the step edge under conditions that enable the system to remain close to thermodynamic equilibrium, i.e., for a sufficiently small detachment rate or external deposition rate. In these cases, the

supersaturation has small values. Linear kinetic law (5.17), with neglect of the corrective flux, f_+ , is found on average to provide a reasonably accurate approximation for the adatom flux at the step edge.

The remaining plots of this section depict situations in which the adatom flux on the right of the step edge may deviate from linear kinetic law (5.17), and thus f_+ may become significant. In particular, Figures 5 and 6 reveal the behavior of the adatom flux versus supersaturation on the right of the step for large enough k or F , respectively. The deviation from the conventional linear behavior predicted by (5.17) is manifested differently in each case.

Let us consider the high-detachment rate cases with zero deposition, as these are depicted in Figure 5. If the supersaturation is sufficiently close to zero, when the flux is small enough, then the flux is approximately linear with supersaturation but with a slope that can be different from the value $D\phi_+a$ predicted by kinetic law (5.17). Farther away from equilibrium, the dependence of adatom flux on supersaturation evidently becomes nonlinear. This nonlinear behavior becomes more pronounced for larger k .

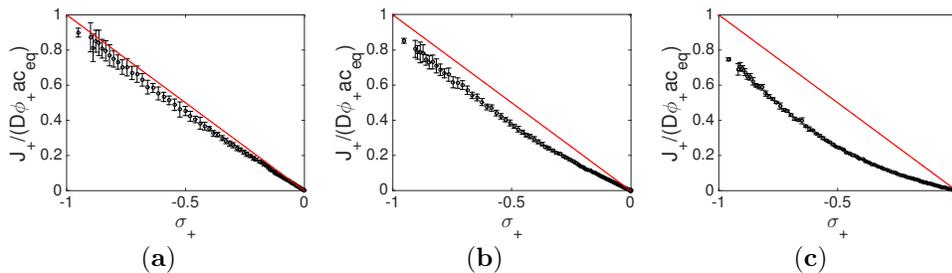


FIG. 5. (Color available online.) Plots of KMC simulations (circles) and the linear kinetic law (red solid line) for adatom flux versus supersaturation on the right of step edge without external deposition ($F = 0$) for different values of detachment factor, k , and fixed parameters $N = 50$, $D = 10^{10}$, and $\phi_{\pm} = 1$. From left to right: (a) $k = 0.04$; (b) $k = 0.09$; and (c) $k = 0.20$. In each plot, the solid line represents linear kinetic law (5.17), by neglect of f_+ . The error bars are determined by use of the standard deviation of flux in 10 ensembles of 10^5 simulations.

Next, consider a small detachment factor, k , but large deposition rate F ; see Figure 6. We observe that for the smallest value of F used in these plots (Figure 6(a)), the flux computed via KMC simulations agrees reasonably well with linear kinetic law (5.17) for a wide range of values for the supersaturation, σ_+ . For larger values of F (Figures 6(b), (c)), the flux remains linear in the density with a slope equal to the predicted value, $D\phi_+a$, as the density approaches its equilibrium value. However, as the supersaturation increases in magnitude, the nonlinear dependence of the flux is noticeable and becomes more pronounced with increasing varied parameter, F . It is worth noting that an increase in the deposition rate F used in KMC simulations beyond the one used in Figure 6(c), even by a factor of two, drastically alters the long-time behavior of the system: apparently, no steady state can be established for sufficiently large F .

As described above, the high- k (with $0 < k < 1$) and high- F cases of Figures 5 and 6, respectively, differ in the way that the effect of corrective flux f_+ is manifested in the observed value of the flux *near equilibrium*. Let us make an effort to qualitatively discuss the origin of this behavior in the context of the atomistic model by resorting to formula (4.7a). The first line in these formulas contains the prefactor k along with a sum over states with one or more adatoms in the lattice site corresponding to the

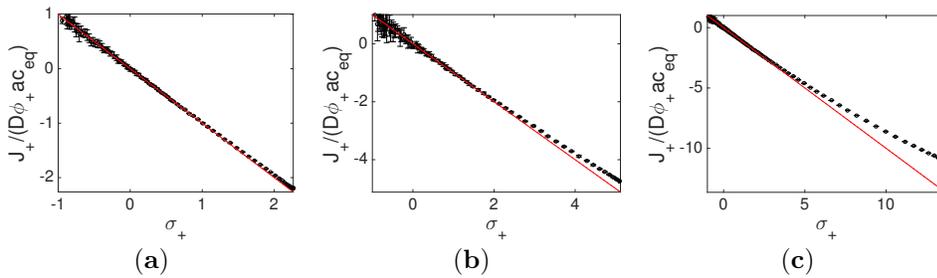


FIG. 6. (Color available online.) Plots of KMC simulations (circles) and the linear kinetic law (red solid line) for adatom flux versus supersaturation on the right of step edge for small yet fixed detachment factor, $k = 2.5 \times 10^{-3}$, and different values of deposition rate F , with fixed parameters $N = 50$, $D = 10^{10}$, and $\phi_{\pm} = 1$. From left to right: (a) $F = 10^8$ ($\epsilon = 10^{-2}$); (b) $F = 2 \times 10^8$ ($\epsilon = 2 \times 10^{-2}$); and (c) $F = 4 \times 10^8$ ($\epsilon = 4 \times 10^{-2}$). The solid line represents linear kinetic law (5.17), by neglect of f_+ , in each plot. The error bars are determined using the standard deviation of flux in 10 ensembles of (a) 10^6 simulations; and (b), (c) 10^5 simulations.

edge atom. This set of configurations does *not* allow for atom detachment; thus, according to this contribution to f_+ , the change of the flux with supersaturation should be suppressed. This prediction should explain the behavior of the slope of the flux versus supersaturation as shown in Figure 5. The remaining terms in (4.7a) come from two- or higher-particle states, which furnish significant contributions if k or F is sufficiently large. These remaining corrections account for configurations in which attachment is inhibited, thus causing an overall increase of the flux out of the step. This prediction is consistent with Figure 6.

We have been unable to explicitly express the corrective fluxes, $f_{\pm}(t)$, as a function of adatom densities $c_{\pm 1}(t)$ on the basis of the analytical model. In order to quantify the nonlinear behavior of the flux near the step edge, we fit the fluxes computed by KMC simulations to polynomials of $\sigma_+ = c_1/c^{eq} - 1$. Figure 7 shows the fitted flux in two cases where deviations are significant: high k with small F , and high F with small k . In each case, a quadratic polynomial of supersaturation appears to adequately capture the behavior of the flux versus supersaturation.

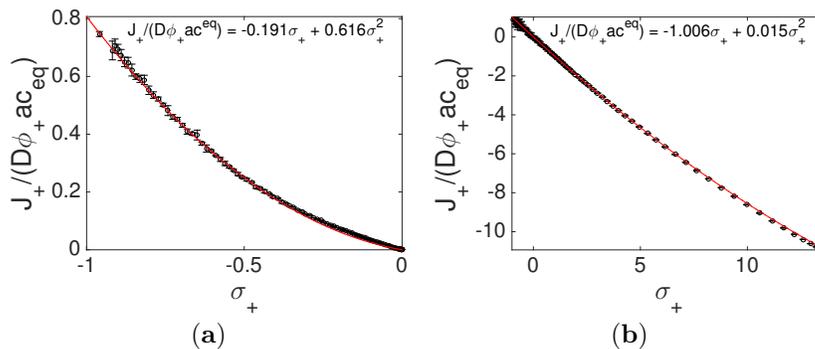


FIG. 7. (Color available online.) Plots of KMC simulations (circles) and fitted quadratic polynomials of σ_+ (red solid line) for adatom flux versus supersaturation on the right of step edge, for high detachment rate or high deposition rate. The fixed parameters are $N = 50$, $D = 10^{10}$, and $\phi_{\pm} = 1$. From left to right: (a) $k = 0.20$ with $F = 0$; and (b) $k = 2.5 \times 10^{-3}$ with $F = 4 \times 10^8$. In each plot, the widths of the error bars are determined by use of the standard deviation of flux in 10 ensembles of 10^5 simulations.

We conclude that a linear kinetic relation for the adatom flux at the step edge in principle does *not* suffice to capture the full range of phenomena displayed by the atomistic solid-on-solid model. Instead, it is more reasonable to propose a discrete expansion of the form

$$(6.1) \quad \mp J_{\pm} \approx c^{eq} \sum_{n=1}^{N_*} B_{\pm}^{(n)} \sigma_{\pm}^n,$$

where the number, N_* , would be speculated empirically. At the mesoscale, the corresponding nonlinear kinetic relation for the flux at the step edge is provided by (1.1). A systematic derivation of this relation from the atomistic model is still elusive.

Remark 6.1. Based on our KMC results, we expect that (6.1) reasonably reduces to conventional linear kinetic relation (2.11) if

$$(6.2) \quad \mathcal{A} := k + \frac{\epsilon}{\phi_+ + \phi_-} \ll 1.$$

This empirical criterion appears less restrictive on ϵ than estimates (5.1) and (5.2), suggesting that the bounds in Proposition 5.1 may be improved; see Remark 5.2. Accordingly, if \mathcal{A} is large enough, then (nonlinear) terms with $n \geq 2$ should become significant.

In our KMC simulations, we observe that the linear kinetic relation for the adatom flux is reasonably accurate if the quantity \mathcal{A} , defined by (6.2), does not exceed 0.01.

7. Discussion and conclusion. Starting with a simplified atomistic solid-on-solid-type model in 1D, we studied the effect of the steric hindrance associated with the pile-up of adatoms on the mesoscale description of single-step motion. We placed emphasis on the relation between the adatom flux and density at the step edge. Our approach relied on a combination of a master equation for adatom states, in the context of an analytical model, and KMC simulations in 1D. A noteworthy result was our heuristic derivation from the master equation of exact formulas for the adatom flux; these indicate the physical origin, in terms of atomistic transitions, of corrections to the linear kinetic relation of the BCF model. Furthermore, by using a property (Proposition 3.1) inherent to the marginalized master equation, as well as perturbation theory and asymptotics for sufficiently small external deposition flux, F , we estimated the aforementioned corrections for small lattice spacing. By KMC simulations, we also observed deviations of the behavior of the flux from the conventional (linear-in-density) prediction of the BCF model.

The master equation approach in this paper forms a nontrivial extension of the analytical model invoked in [20, 19]. By including material deposition onto the surface from above, we accounted for adatom states that do not conserve the total mass of the system. In the course of our analysis, we formally showed that the system has a steady state only for sufficiently small external deposition flux.

Our 1D atomistic model captures a few fundamental elements of diffusion processes on crystal surfaces below the roughening transition. In particular, the model describes hopping of adatoms, and, most importantly, attachment/detachment of atoms at the step in the absence of kinks. The 1D character of the model certainly poses a few limitations, as mentioned in the introduction (section 1). For example, nucleation cannot be included in our analysis.

Physically, however, our approach illustrates an adatom-mediated mechanism of steric hindrance to step motion. Therefore, we believe that our results could shed

light on recent, experimental observations of diffusion on ice surfaces [23, 3]. These experiments have shown that large concentrations of noncrystalline molecules are kinetically stabilized by external material deposition. Our nonlinear kinetic law at the step edge suggests a general mechanism that could explain the stability of such states. In particular, when $\kappa_{\pm}^{(2)} < 0$ in (1.1) (corresponding to the coarse-grained model at hand), low deposition rates can lead to greater adatom concentrations than those predicted by the linear theory alone. Physically, we interpret this excess concentration to be kinetically stabilized by the steric-blocking effect, which inhibits adatom attachment events. Viewed differently, the existence of a steady state implies that the step velocity is equal to FL (by mass conservation), where L is the average terrace width; this velocity is independent of coefficient $\kappa_{\pm}^{(2)}$. But the condition $\kappa_{\pm}^{(2)} < 0$ amounts to an additional resistance to attachment, so that more adatoms are needed at the step edge, relative to the linear theory, to ensure a constant step velocity.

A possible criticism of our modeling concerns the structure of the corrective fluxes, f_{\pm} . This structure appears to be specific to the 1D character of our model. Admittedly, in our approach these correction terms are only associated with rules for attachment and detachment of atoms at the step from/to the terrace. Thus, we leave out the effect of kinks, which is expected to partially alter the mass flux since kink sites can act as local sources or sinks for atoms [6]. Because of kinks, the local curvature of the step is expected to affect the equilibrium adatom density in a 2D mesoscale setting, giving rise to the step stiffness. The derivation of this effect from a fully atomistic model was not addressed here. In spite of these complications, it is reasonable to expect that our 1D model captures features of 2D step motion if kinks are sufficiently far apart from each other, that is, if the kink density is small.

In this vein, it is natural to ask the following question: Would it be possible to physically improve our one-step atomistic model by retaining its 1D character yet enriching it with effects that become significant for low *and* high supersaturations? A possibility is to account for pair correlations of adatoms due to their energetic interactions. The next stage in this direction would be to consider two steps by including entropic and elastic step-step interactions in the modeling. This task requires appropriate discretization of elastic effects on the lattice. Another scenario that could be examined in the 1D setting is the process of step permeability, which thus far is modeled phenomenologically at the mesoscale [17]. Since our model does not describe processes by which adatoms may pass from one side of the step to the other without attaching to the step edge, it seems that permeability is not inherent in our treatment.

In this work, we focused on averages for the adatom density, step position, and adatom flux, motivated by the known structure of the BCF model. Hence, we have not addressed the stochastic fluctuations arising in step motion. We believe that this stochastic effect should be more pronounced at high enough supersaturations. The step fluctuations are known to be intimately connected to step stiffness [11]; thus, a 2D atomistic model would be a natural starting point for a systematic study.

Appendix A. On birth-death processes. In this appendix, we use a toy model for the birth-death Markov process (see, e.g., [13]) to indicate that no steady state of the master equation exists for large enough external deposition flux, F .

A birth-death process is a Markov process with infinitely many states, labeled by $n = 0, 1, \dots$, for which transitions are only allowed between the n th and $(n + 1)$ st states. Our discrete KRSOS model has this structure if we classify configurations α by the number of adatoms on the terrace, i.e., by the cardinality $|\alpha| = n$ for $n = 0, 1, \dots$. For our purposes, the detachment and deposition-from-above events

correspond to births, while attachment events correspond to deaths.

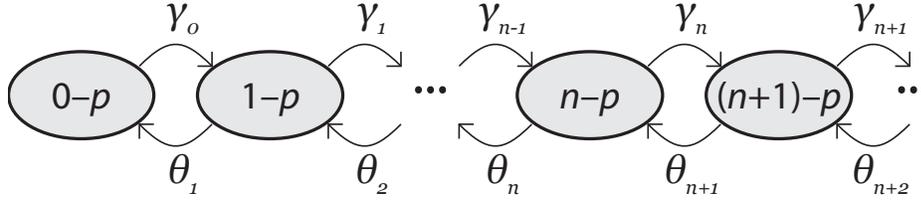


FIG. 8. Schematic of the birth-death process showing the hierarchy of particle states and respective transitions. The arrows connecting successive states depict the underlying Markovian character of transitions. The symbol “ n - p ” stands for the n -particle state; γ_n denotes the transition from the n -particle to the $(n + 1)$ -particle state; and θ_n is the rate for the transition from the n -particle state to the $(n - 1)$ -particle state.

Let γ_n denote the rate for the transition from the n -particle state to the $(n + 1)$ -particle state (the process of “birth”) and θ_n denote the rate for the transition from the n -particle state to the $(n - 1)$ -particle state (“death”); see Figure 8. If p_n^{ss} is the steady-state probability of the n -particle configuration, we have the following balance equations:

$$(A.1) \quad \begin{aligned} \gamma_n p_n^{ss} &= \theta_{n+1} p_{n+1}^{ss}, \\ \gamma_0 p_0^{ss} &= \theta_1 p_1^{ss}. \end{aligned}$$

Solving (A.1) for p_n^{ss} , we find the formula

$$(A.2) \quad p_n^{ss} = \frac{\gamma_n \gamma_{n-1} \cdots \gamma_0}{\theta_{n+1} \theta_n \cdots \theta_1} p_0^{ss},$$

which of course must satisfy the normalization constraint $\sum_{n=0}^{\infty} p_n^{ss} = 1$. This constraint can be written as

$$(A.3) \quad p_0^{ss} \sum_{n=0}^{\infty} \frac{\gamma_n \gamma_{n-1} \cdots \gamma_0}{\theta_{n+1} \theta_n \cdots \theta_1} < \infty.$$

In other words, if condition (A.3) does not hold, the probabilities in (A.2) are not normalizable, and, thus, no steady state exists.

In our setting of epitaxial growth in 1D, the rates γ_n and θ_n are determined by the transition rates for attachment, detachment, and deposition. These rates satisfy the following equations:

$$(A.4) \quad \begin{aligned} \gamma_n &= \frac{1}{p_n^{ss}} \sum_{|\alpha|=n} \{F + Dk(\phi_+ + \phi_-) \mathbb{1}(\nu_{-1}(\alpha) = 0)\} p_{\alpha}^{ss} \\ &= F + Dk(\phi_+ + \phi_-) a_n, \end{aligned}$$

$$(A.5) \quad \begin{aligned} \theta_n &= \frac{1}{p_n^{ss}} \sum_{|\alpha|=n} \{D\phi_+ \mathbb{1}(\nu_1(\alpha) = 1) + D\phi_- \mathbb{1}(\nu_1(\alpha) = 0) \\ &\quad \times \mathbb{1}(\nu_1(\alpha) > 0)\} p_{\alpha}^{ss} \\ &= D\phi_+ b_n + D\phi_- d_n, \end{aligned}$$

where a_n , b_n , and d_n are the probabilities of n -particle configurations that forbid detachment, attachment from the right, and attachment from the left, respectively. By (A.4) and (A.5), the ratio of birth and death rates is bounded below; i.e., we have the inequality

$$(A.6) \quad \frac{\gamma_n}{\theta_{n+1}} \geq \frac{F}{D(\phi_+ + \phi_-)} \quad (n = 0, 1, \dots).$$

We deduce that the condition $F > D(\phi_+ + \phi_-)$ implies that no steady state may exist because normalization condition (A.3) is violated. In the context of the 1D epitaxial system, having $F > D(\phi_+ + \phi_-)$ means that the deposition rate is faster than the attachment rate. In this case, the number of particles on the terrace constantly grows, and, hence, no steady state can be established.

Appendix B. On steady-state solution: Asymptotics of inverse Laplace transform. In this appendix, we derive formula (3.7) for the steady-state probability density. Our derivation relies on the following. (i) We assume that $\epsilon = F/D$ is sufficiently small so that $[I - \epsilon V \mathfrak{D}(s) V^{-1} \mathfrak{B}]^{-1}$ exists and can be written as $\sum_{n=0}^{\infty} [\epsilon V \mathfrak{D}(s) V^{-1} \mathfrak{B}]^n$; and (ii) the quantity \mathbf{p}^{ss} , which is the limit of $\mathbf{p}(t)$ as $t \rightarrow \infty$, comes from contributions to the inverse Laplace transform of (3.6) corresponding to the pole at $s = \lambda_1 = 0$ in the Laplace complex (s -) domain. Recall that $\mathfrak{D}(s) := \text{diag}\{(s - D\lambda_j)^{-1}\}_{j=1}^{\Omega(M)}$, where λ_j are the eigenvalues of matrix \mathfrak{A} of the deposition-free problem. For a review of the Laplace transform, see [24].

Let us now elaborate on these ideas. From (i) we may write $\mathbf{p}(t)$ as

$$(B.1) \quad \begin{aligned} \mathbf{p}(t) &= \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} \sum_{n=0}^{\infty} (\epsilon V \mathfrak{D}(s) V^{-1} \mathfrak{B})^n V \mathfrak{D}(s) V^{-1} \mathbf{p}(0) e^{st} ds \\ &= \frac{1}{2\pi i} \sum_{n=0}^{\infty} \epsilon^n V \mathcal{I}_n(t) V^{-1} \mathbf{p}(0), \end{aligned}$$

where γ is a positive constant and the integrals $\mathcal{I}_n(t)$ are defined by

$$(B.2) \quad \mathcal{I}_n(t) = \int_{\gamma-i\infty}^{\gamma+i\infty} (\mathfrak{D}(s) \tilde{\mathfrak{B}})^n \mathfrak{D}(s) e^{st} ds; \quad \tilde{\mathfrak{B}} := V^{-1} \mathfrak{B} V.$$

The integrand in (B.2) is a matrix resulting from the product $(\mathfrak{D} \tilde{\mathfrak{B}})^n \mathfrak{D}$, whose entries have the form

$$(B.3) \quad \left[(\mathfrak{D} \tilde{\mathfrak{B}})^n \mathfrak{D} \right]_{ij} = \frac{\tilde{b}_{ik_1} \tilde{b}_{k_1 k_2} \cdots \tilde{b}_{k_{n-2} k_{n-1}} \tilde{b}_{k_{n-1} j}}{(s - \lambda_i)(s - \lambda_{k_1}) \cdots (s - \lambda_{k_{n-1}})(s - \lambda_j)};$$

\tilde{b}_{kl} are appropriate coefficients independent of the Laplace variable, s .

By (ii) above, since we seek the steady-state solution, \mathbf{p}^{ss} , the main contribution to integral (B.2) comes from the pole at $s = \lambda_1 = 0$. The only terms which include $(s - \lambda_1)^{-1}$ are those with $j = 1$ in (B.3). This conclusion can be reached after simplification in the algebra, which is described as follows. The rows of the matrix V^{-1} contain the left-eigenvectors of matrix \mathfrak{A} . Because probability is conserved, so that the column sums of \mathfrak{A} and \mathfrak{B} are zero, we have $(V^{-1})_{1i} = (V^{-1})_{1j}$ for all i, j . The matrix $V^{-1} \mathfrak{B}$, which forms the left matrix product in the $\tilde{\mathfrak{B}}$ of (B.2), must obey

$$(B.4) \quad \sum_i (V^{-1})_{1i} (\mathfrak{B})_{ij} = 0 \quad \text{for all } j.$$

Hence, the right-hand side of (B.3) vanishes if any of the indices $i, k_1, k_2, \dots, k_{n-1}$ is equal to unity. Consequently, the steady-state contributions to integral (B.2) come only from simple poles at $s = \lambda_1$, specifically the terms in (B.3) for which $j = 1$.

If $n = 0$, (B.2) equals $e^{Dt\Lambda}$, the inverse transform of $\mathfrak{D}(s)$. If $n > 0$, an asymptotic expansion for $\mathcal{I}_n(t)$ as $t \rightarrow \infty$ may be computed using the residue theorem, viz.,

$$\begin{aligned}
 [\mathcal{I}_n(t)]_{ij} &= \int_{\gamma-i\infty}^{\gamma+i\infty} [(\mathfrak{D}\tilde{\mathfrak{B}})^n \mathfrak{D}]_{ij} e^{st} ds \\
 &= \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{\tilde{b}_{ik_1} \tilde{b}_{k_1 k_2} \cdots \tilde{b}_{k_{n-2} k_{n-1}} \tilde{b}_{k_{n-1} j}}{(s - \lambda_i)(s - \lambda_{k_1}) \cdots (s - \lambda_{k_{n-1}})(s - \lambda_j)} e^{st} ds \\
 &\approx 2\pi i \sum_{i, k_1, k_2, \dots, k_{n-1} \neq 1} \frac{\tilde{b}_{ik_1} \tilde{b}_{k_1 k_2} \cdots \tilde{b}_{k_{n-2} k_{n-1}} \tilde{b}_{k_{n-1} 1}}{(-\lambda_i)(-\lambda_{k_1}) \cdots (-\lambda_{k_{n-1}})} \\
 \text{(B.5)} \quad &= \begin{cases} 2\pi i [(-\Lambda^\dagger \tilde{\mathfrak{B}})^n]_{i1}, & j = 1, \\ 0, & j > 1, \end{cases}
 \end{aligned}$$

as $t \rightarrow \infty$. In the above calculation, the symbol \approx implies that the respective result of contour integration leaves out contributions from poles other than $s = \lambda_1$ in the limit $t \rightarrow \infty$. For the same reason, all entries in the matrix $\mathcal{I}_n(t)$ other than the first column are asymptotically small and are neglected.

Finally, by substitution of asymptotic formula (B.5) into (B.1), we compute the steady-state probability distribution as

$$\begin{aligned}
 \mathbf{p}^{ss, \epsilon} &= \sum_{n=0}^{\infty} \epsilon^n V \left(-\Lambda^\dagger \tilde{\mathfrak{B}} \right)^n [\mathbf{e}_1, \mathbf{0}, \mathbf{0}, \dots, \mathbf{0}] V^{-1} \mathbf{p}(0) \\
 \text{(B.6)} \quad &= \sum_{n=0}^{\infty} (-\epsilon \mathfrak{A}^\dagger \mathfrak{B})^n \mathbf{p}^0,
 \end{aligned}$$

which leads to (3.7). In the above, we used the definition $\tilde{\mathfrak{B}} = V^{-1} \mathfrak{B} V$ along with $\mathfrak{A}^\dagger = V \Lambda^\dagger V^{-1}$. Equation (B.6) is written in terms of the equilibrium distribution, \mathbf{p}^0 , which satisfies (3.3) when $\epsilon = 0$. This distribution can be derived in the same way as (3.2), or computed as $\mathbf{p}^0 = \lim_{t \rightarrow \infty} \exp(D\mathfrak{A}t) \mathbf{p}(0) = V[\mathbf{e}_1, \mathbf{0}, \mathbf{0}, \dots, \mathbf{0}] V^{-1} \mathbf{p}(0)$, where \mathbf{e}_1 is the $\Omega(M)$ -dimensional vector $\mathbf{e}_1 = (1, 0, 0, \dots, 0)^T$.

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