Breakdown of metastable step-flow growth on vicinal surfaces induced by nucleation

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We consider the growth of a vicinal crystal surface in the presence of a step-edge barrier. For any value of the barrier strength, measured by the length $\ell_{\text{ES}}$, nucleation of islands on terraces is always able to destroy asymptotically step-flow growth. The breakdown of the metastable step-flow occurs through the formation of a mound of critical width proportional to $L_c \sim 1/\ell_{\text{ES}}$, the length associated to the linear instability of a high-symmetry surface. The time required for the destabilization grows exponentially with $L_c$. Thermal detachment from steps or islands, or a steeper slope increase the instability time but do not modify the above picture, nor change $L_c$ significantly. Standard continuum theories cannot be used to evaluate the activation energy of the critical mound and the instability time. The dynamics of a mound can be described as a one dimensional random walk for its height $k$: attaining the critical height (i.e. the critical size) means that the probability to grow ($k \to k+1$) becomes larger than the probability for the mound to shrink ($k \to k-1$). Thermal detachment induces correlations in the random walk, otherwise absent.

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I. INTRODUCTION

The growth process of a crystal surface by deposition of particles resembles in many respects a phase separation process. The role of the order parameter is played by the local slope $u$, whose average value $m$ is fixed by the orientation of the substrate where deposition occurs. A uniform orientation is often not stable for a growing crystal, for thermodynamic as well as for kinetic reasons: As deposition proceeds the flat profile gives way to a rough surface, with the formation and growth of mounds. The first stages of the destabilization process may occur through the appearance of large wavelength undulations or the formation of localized perturbations: the former happens if the orientation $m$ is linearly unstable, the latter if it is metastable. By varying $m$ it is therefore possible to pass from one regime to another, much in the same way as it is possible to go, in the phase separation of a binary alloy, from spinodal decomposition to droplet nucleation by changing the relative concentration.

In the context of crystal growth, the unstable regime corresponds to a high-symmetry orientation, the counterpart of a symmetric quenching for a binary alloy. This regime has been studied in dozens of papers and similarities and differences with phase separation processes have been highlighted. In the following we study the so called vicinal regime when the slope $m$ is sufficiently far from a high symmetry orientation: in this case the surface is made up of small terraces separated by steps and most of the deposited atoms attach to preexistent steps (step-flow growth). This regime is the counterpart of the case where, for a binary mixture, the homogeneous phase is metastable, but it can be disrupted by the nucleation and growth of droplets of the stable phase.

In the system considered in this paper, the key atomistic ingredient of the destabilization is the presence of an energetic step-edge or Ehrlich-Schwoebel (ES) barrier that hinders the descent of atoms from upper to lower terraces. This instability has a purely kinetic origin, due to the nonequilibrium character of the growth process. The analytical investigation of a growing vicinal profile reveals two possible linear instabilities: step-bunching (the uniform density of steps is unstable) and step-meandering (straight steps are unstable). Step-edge barriers make the surface stable with respect to the bunching and unstable with respect to the meandering. This picture does not exhaust all the possibilities, because mound formation may occur also via nonlinear mechanisms, leading to a late stage morphology which does not differ from what is obtained by growing on a (linearly unstable) high symmetry orientation. Two paths leading to mounding can be anticipated: atomistic nucleation on terraces and defect formation, due to nonlinear meandering. In the following we consider the first possibility, which is the natural mechanism for two reasons: in the first place, it is solely responsible for destabilization if steps keep straight; secondly, it is
the correct process to consider if we want to study the
crossover from the unstable to the metastable regime,
because atomistic nucleation plus step-edge barriers are
responsible for destabilizing both a high symmetry and a
vicinal surface.

Since our interest is the destabilization via atomistic
nucleation, we will consider a one-dimensional surface.
This model may apply to a two-dimensional surface when
steps are straight (see the final section for additional
Remarks).

Let us now summarize the main features of the desta-
bilization mechanism and our principal results. Freshly
deposited atoms (adatoms) diffuse on terraces, generally
until they are incorporated at steps. From time to time
two of them meet and an atomistic nucleation occurs.
Since the vicinal flat profile is linearly stable, the nu-
cleated dimer is generally swept by the advancing steps.
Only once in a while another nucleation event takes place
on top of the dimer before it is reabsorbed, generating a
very small mound. A mound may grow larger, but in
general it tends to disappear, unless, by a fluctuation, it
reaches a critical size such that it becomes more likely
for it to grow rather than to shrink. At this point the
flat profile is destabilized and it is not recovered by the
dynamics. A crucial role is hence played by the critical
nucleus, the localized perturbation of the profile (mound)
that separates small perturbations that tend to be reab-
sorbed from large ones that grow irreversibly.

Section II highlights the inadequacy of atomistic ap-
proaches based on the assumption that the critical nu-
cleus has a fixed size, independent of the ES barrier. Sec-
tion III shows that also the application of traditional con-
tinuum methods for studying the breakdown of metastabi-
ity fails in our case. In Section IV we discuss the form
of the unstable current, which allows to distinguish be-
tween the unstable and the metastable regime and gives
insight into the crossover connecting them.

In Secs. V A and V B we present the results of Ki-
netic Monte Carlo simulations showing that the surface
is metastable for any strength of the additional step-edge
barrier and that the instability time diverges exponen-
tially for decreasing barrier. We also show that when the
slope is sufficiently small we have a crossover to the
linearly unstable regime, where the instability time diver-
ges as a power-law with the barrier. Secs. V C and V D present an analysis of the properties of the critical
nucleus, whose width is related to the instability of a
singular surface, along with a detailed study of how the
nucleus is dynamically generated, allowing a quantitative
derivation of the instability time.

Finally, in Sec. VII the global physical picture is
shown to be robust when thermal detachment is allowed:
metastability holds for any barrier strength also in this
case. Nonetheless, we show that thermal detachment has
nontrivial effects on the development of the critical nu-
cleus and this results in a remarkable increase of the
instability time. A discussion (Sec. VII) concludes the
paper.

In a recent Letter we have presented some partial
results of this line of research. Though some overlap is
unavoidable, we have minimized it in the present paper
by referring to the Letter when needed and focusing here
on completely new results: the failure of the continuum
approach (Sec. III); the study of the crossover between
singular and vicinal regimes (Sec. IV); the detailed nu-
merical and analytical investigation of the destabiliza-
process at the atomistic level (Secs. V C V D and the
Appendix); the simulations with thermal detachment
(Sec. VII).

II. THEORY WITH A CRITICAL NUCLEUS OF
FIXED SIZE

A simple and appealing argument for analyzing the
destabilization of step-flow on vicinal surfaces has been
recently introduced by Kalhunki and Krug9,12 and it is
based on the idea that the critical nucleus is a mound of
height two. The stability or instability of step-flow is
therefore assessed by evaluating whether such a nucleus
is formed or not by the dynamics. This is performed
by comparing the mean timescales of the two processes
that can occur once an island is formed on a vicinal ter-
race: either the island is reabsorbed by the advancing step (and this requires a time \( t_{\text{m}} \)) or a second-layer nu-
cleation event takes place on top of it (this occurs over a
time \( t_{\text{2nd}} \)). If \( t_{\text{2nd}} < t_{\text{m}} \), a mound of height two is formed and this leads to the destabilization of the surface.

There are several ways of implementing in practice this
criterion and they all lead to results that are equivalent,
apart from small differences in the numerical factors. We
refer here to the simplest model of epitaxial growth, with
deposition occurring at rate \( F \), adatom diffusion at rate \( D \) and the strength of the ES barrier quantified by the
length \( l_{\text{ES}} = D/D'-1 \), where \( D' \) is the interlayer diffusion
coefficient. One way to implement the criterion is to impose that the mean number of second-layer nucleation
events occurring during the deposition of a monolayer is
larger than 1. The number of such nucleation events can
be evaluated by integrating the second-layer nucleation
rate \( \omega \) over time up to \( 1/F \),

\[
N_{\text{nuc}}(t = 1/F) = \int_{0}^{1/F} ds \omega[R(s)],
\]

where \( R(s) \) is the size of the island at time \( s \) and

\[
\omega[R] = \kappa \frac{F^2 R^4}{12D'} \left( 1 + \frac{l_{\text{ES}}}{R} \right),
\]

(\( \kappa \) being a constant of the order of one,13,14 that will be
neglected in the following).

Assuming that half of the deposited adatoms con-
tribute to the growth of the island (and the other half
is incorporated at the advancing steps), we have \( R(s) = F\ell s/2 \), where \( \ell = 1/m \) is the size of the vicinal terrace.
Performing the integrals and imposing $N_{\text{nuc}}(t = 1/F) > 1$, we obtain
\[ \ell_{\text{ES}} > \ell_{\text{ES}}^c = \frac{6D/F}{\ell^3} - \frac{1}{15} \ell. \] (3)

We stress again that other implementations of the same criterion yield virtually identical results. For instance one can impose that the probability $p_{\text{nuc}}(t^*)$ that second-layer nucleation occurs within a time $t^* = 1/(2F)$ after the creation of the island is larger than $1/2$. In this way we obtain the same condition $\mathbf{K}$ except for a factor $\ln(2)$ multiplying the first term on the r.h.s..

We conclude that the assumption of a critical nucleus of height two implies the existence of a threshold: for small enough barrier, step-flow growth should be fully stable with respect to the nucleation of mounds. As shown below, this prediction is in striking contrast with numerical simulations, showing that, even for values of $\ell_{\text{ES}}$, the surface is in fact metastable. This is a clear indication that something in the argument just presented is not correct.

One could think that a higher critical nucleus would fix the problem. However, a critical nucleus of fixed height $k_c$ would always imply the existence of a range of small values of $\ell_{\text{ES}}$ for which step-flow growth is fully stable. This can be seen by considering that, for any $k_c$, the condition for instability is of the form $A(\ell_{\text{ES}}) > A_0$, where $A$ is a growing function of $\ell_{\text{ES}}$, expressing how likely the formation of the critical nucleus is, and $A_0$ is a constant, whose precise value depends somewhat arbitrarily on the details of the implementation. If $A(\ell_{\text{ES}} = 0) > A_0$ then the growth would be unstable even for $\ell_{\text{ES}} = 0$ and this is absurd. Hence $A(\ell_{\text{ES}} = 0)$ must be smaller than $A_0$ and this implies that in an interval of small $\ell_{\text{ES}}$ growth is stable. Metastability down to $\ell_{\text{ES}} = 0$ would be possible only if $A(\ell_{\text{ES}} = 0)$ exactly equals $A_0$, but this is impossible, given that a precise value of $A_0$ cannot be unambiguously defined.

Another reason for the failure of the atomistic argument discussed above could be that comparing the average values of $t_{\text{2nd}}$ and $t_{\text{adv}}$ is not appropriate, we should consider instead their full distributions $P_2(t_{\text{adv}})$ and $P_2(t_{\text{2nd}})$. The surface is unstable if there is a finite probability that $t_{\text{2nd}} < t_{\text{adv}}$, i.e. if

\[ p_{t_{\text{2nd}} < t_{\text{adv}}} = \int_0^\infty dt_{\text{2nd}} P_2(t_{\text{2nd}}) \int_{t_{\text{2nd}}}^\infty dt_{\text{adv}} P_1(t_{\text{adv}}) > 0. \] (4)

Let us now consider the limit $\ell_{\text{ES}} \to 0$: both distributions have a well defined limit, because the nucleation rate on top of a terrace and the velocity of a step reach finite values for $\ell_{\text{ES}} = 0$. Since $P_2(t_{\text{2nd}}) > 0$ for small but finite $t_{\text{2nd}}$, the quantity $p_{t_{\text{2nd}} < t_{\text{adv}}}$ is always greater than zero. In simple terms, considering the condition $\mathbf{K}$ for metastability leads to the wrong conclusion that the vicinal surface should be destabilized for $\ell_{\text{ES}} = 0$ as well. In conclusion, the hypothesis of a critical nucleus with fixed height is not compatible with numerical results and known properties for $\ell_{\text{ES}} = 0$. As it will be shown below, the diverging size of the critical nucleus is the crucial element of the breakdown of metastable step-flow growth.

### III. CONTINUUM CAHN-HILLIARD THEORY FOR THE METASTABILITY

The goal of this section is to study the metastability by applying the Cahn-Hilliard (CH) theory developed for ordinary phase-separation to a minimal continuum model for epitaxial growth. We will show that this approach is completely unable to explain the dynamical behavior of the growing surface even in qualitative terms. A very short introduction to the continuum approach is given in the next two paragraphs.

In the absence of events which do not conserve matter (evaporation) or volume (formation of overhangs), the dynamics of a one-dimensional growing crystal surface is described by $\partial_t z = -\partial_x J$, where $J$ is the current describing all microscopic processes occurring at the surface and $z$ is the local height $h$ with respect to a comoving frame, $z = h - Ft$ ($F$ is the flux intensity). Since we are not studying phenomena depending on the substrate-adsorbate interaction, $J$ can be safely assumed to depend only on spatial derivatives of $z$, $u = z', u', u''$, . . . . In the next section we will evaluate numerically the slope dependent current, $j_{\text{ES}}(u)$, also called step-edge or ES current because it is due to asymmetric sticking to steps. $j_{\text{ES}}(u)$ is linear at small slope and attains a maximum for $u = m_0$ and finally decreases. In addition, other terms depending on higher order derivatives contribute to the current $J$. The most important has the form $Ku''$, is called Mullins term, and is due to several microscopic processes: thermal detachment from steps and the random character of nucleation and diffusion. In the following we will consider a minimal model, with $J = Ku'' + \alpha j_{\text{ES}}(u)$. The prefactor $\alpha$ is chosen so that $j_{\text{ES}}(0) = 1$: it might be included in the definition of $j_{\text{ES}}(u)$, but its explicit appearance will be useful later.

Given the form of $J$, the evolution equation for the surface slope $u$ has the form of a generalized CH equation

\[ \partial_t u = -\partial_x^2 [Ku''(x) + \alpha j_{\text{ES}}(u)]. \] (5)

Linear stability analysis of a vicinal surface of slope $m$, $z = mx + \delta z \exp(\omega t + iqt)$ provides the spectrum $\omega(q) = \alpha j_{\text{ES}}^c(m)q^2 - Kq^4$. If $m > m_0$, $j_{\text{ES}}^c(m) < 0$ and the surface is linearly stable; if $m < m_0$ the surface is linearly unstable, the most unstable wavevector (the one for which $\omega(q)$ is maximum) is $q_c = \sqrt{\alpha j_{\text{ES}}^c(m)/2K}$, the most unstable length is $L_c = 2\pi/q_c = 2\pi\sqrt{2K/\alpha j_{\text{ES}}^c(m)}$, and the linear instability emerges after a time $t_c \approx 1/\omega(q_c) \approx K/(\alpha j_{\text{ES}}^c(m))^2$. For small barriers $\alpha$ is proportional to $\ell_{\text{ES}}$: therefore the instability appears with a typical timescale of order $1/\sqrt{\ell_{\text{ES}}}$ and after a typical time of order $1/\ell_{\text{ES}}^2$. These temporal and spatial scales also diverge when $m \to m_0^-$, because $j_{\text{ES}}^c(m) \to 0$. 
Stationary solutions of Eq. (5) are given by $K u''(x) + \alpha j_{ES}(u) = \mu$, where $\mu$ is related to $m$ by the condition $\langle u \rangle = m$. The critical nucleus is a localized steady state, characterized by $u(x) = m$ everywhere except in a region of finite size. This implies that, for the critical nucleus, $\mu = \alpha j_{ES}(m)$ and

$$K u''(x) + \alpha [j_{ES}(u) - j_{ES}(m)] = 0. \quad (6)$$

Rather than reproducing the standard procedure for getting the energy $\Delta F$ of the critical nucleus, we simply remark that rescaling $x$ allows to find how $\Delta F$ depends on $\alpha$ and $K$. If $X = \sqrt{\gamma K} x$, Eq. (5) has the parameter-free form $u_{XX} + [j_{ES}(u) - j_{ES}(m)] = 0$ and the pseudo free-energy $F$ is [such that $\partial_u F = \alpha^2 (\Delta F/\alpha m)$]

$$F = \int dx \left[ \frac{K}{2} (\partial_x u)^2 + \alpha U(u) \right] = \sqrt{\alpha K} \int dX \left[ \frac{1}{2} (\partial_X u)^2 + U(u) \right] \quad (7)$$

where $U'(u) = -j_{ES}(u)$. In conclusion,

$$\Delta F(\alpha, K) = \sqrt{\alpha K} \Delta F(1, 1). \quad (8)$$

In a thermodynamic system, once the activation energy $\Delta F$ has been calculated, the instability time is given by $\tau = \exp(\Delta F/k_B T)$, because the system overcomes the barrier by thermal fluctuations. In the far-from-equilibrium case of a growing surface, fluctuations allowing to system to leave the local minimum have different origins: fluctuations in the flux (shot-noise) and fluctuations in the nucleation and diffusion processes. Their amplitude plays the role of $k_B T$ in the expression for $\tau_m$.

The analytical form of $j_{ES}(u)$, valid for any $u$ and $\ell_{ES}$, is not easy to write, but we need here only the limiting form for vanishing barriers and finite slope. With these caveats, all the $\ell_{ES}$ dependence is contained in the prefactor $\alpha$, which is proportional to $\ell_{ES}$. Hence for fixed slope, the unstable current is linear in the ES length in the limit of small barrier. According to Eq. (8), the activation barrier is therefore an increasing function of $\ell_{ES}$, the opposite of what is expected and observed! This surprising result cannot be changed by taking into account the possible effects of $\ell_{ES}$ on the noise amplitude, because nucleation noise has a finite limit for $\ell_{ES} = 0$. We must conclude that the continuum minimal model, Eq. (5), is not appropriate for the study of the breakdown of step-flow growth. Additional comments are deferred to the Conclusions.

**IV. CROSSOVER FROM SINGULAR TO VICINAL FOR A TILTED SURFACE**

Before reporting the results of a numerical study of the breakdown of step-flow growth, let us discuss what occurs at the boundary between singular and vicinal surface orientations. Linear stability analysis predicts two distinct types of dynamical behavior, depending on how large is the average global tilt $m$ with respect to the value $m_0$ for which the Ehrlich-Schwob equilibrium current $j_{ES}$ is maximal. For $m < m_0$ (singular surfaces) a flat profile is linearly unstable for $q < q_c$ (see the previous section). For $m > m_0$ instead (vicinal surfaces), perturbations of small amplitude decay, since the flat profile is linearly stable, and, if any destabilization occurs, this has to be triggered by fluctuations of sufficiently large amplitude.

In order to study the way the destabilization of vicinal surfaces takes place, it is therefore crucial to check that the surface considered is effectively vicinal, i.e., its slope is larger than $m_0$. This point is made complicated by the fact that $m_0$ may in principle (and it actually does) depend on $\ell_{ES}$, so that it may happen that a surface with fixed $m$ is singular or vicinal depending on the value of $\ell_{ES}$. The variation of $m_0$ is not expected to be large, because the form of the current predicts that the ES current is maximal for finite slopes of the order of $1/\ell_0$ (see Ref. 2) for both $\ell_{ES} \to 0$ and $\ell_{ES} \to \infty$ ($m_0^0$ and $m_0^\infty$, respectively). In any case, this effect must be taken into account for a detailed understanding of the destabilization process. For this reason we have numerically evaluated the form of the nonequilibrium current $j_{ES}(u)$, by measuring, for the KMC model described below, the imbalance in the number of hops toward left or right that adatoms take during the growth of the first few monolayers. More precisely, if $N_l$ and $N_r$ are the number of steps toward left and right, respectively, then the current is

$$j_{ES} = \frac{|N_l - N_r|}{N_{ad}}, \quad (9)$$

where $N_{ad}$ is the number of adatoms deposited.

The results, reported in Fig. 1, display a very slow crossover between $m_0 \approx 0.07$ for small $\ell_{ES}$ and $m_0 \approx 0.03$ for the largest value of $\ell_{ES}$ we could consider: we stress that $m_0$ varies by a factor two against a variation of $\ell_{ES}$ over five orders of magnitude. As expected, these values are of the order of $1/\ell_0 \approx 0.025$.

We can conclude that three types of behavior exist for the system under consideration (Fig. 2). For $m < m_0^\infty \approx 0.03$ the surface is singular (hence linearly unstable) for all values of the ES barrier. For $m > m_0^0 \approx 0.07$ the surface is always linearly stable and metastability can be studied down to $\ell_{ES} \to 0$. For intermediate slopes the surface is vicinal for large $\ell_{ES}$, while it becomes linearly unstable as $\ell_{ES}$ is decreased. In this case a crossover is expected in the way the instability time depends on $\ell_{ES}$.

Notice that the value $m = 1/15 \approx 0.067$ considered in the following sections just falls within this interval. It is important to remark (Sec. III) that the linear instability for a singular surface does not imply that the instability develops immediately. The time required for a sizeable amplification of the initial fluctuations depends on $m$ and it diverges for $m \to m_0$ or $\ell_{ES} \to 0$. 


V. KINETIC MONTE CARLO SIMULATIONS

A. The model

We perform Kinetic Monte Carlo (KMC) simulations of the simplest model for epitaxial growth in $d = 1$. The surface is represented by a set of integer height variables $h_i$, defined on a one-dimensional lattice of $L$ sites. An average tilt $m$ is imposed through helical boundary conditions, $h_{i+L} = h_i + mL$. The average terrace size is thus $\ell = 1/m$. The initial condition is a regular train of steps, $h_i = \lfloor \frac{i}{m} \rfloor$, where $[x]$ is the integer part of $x$. Deposition ($h_i \to h_i + 1$) occurs at rate $F$ on randomly selected sites. Singly bonded atoms (adatoms) attempt diffusion hops to nearest neighbor sites, at rate $D$ if the neighbor belongs to the same terrace of the first site, at rate $D' < D$ (because of the Ehrlich-Schwoebel effect) if the atom must descend a step. Dimers and larger islands are immobile. Thermal detachment is possible at rate $R_d$. When a particle is detached from a step or an island it is placed on the lower terrace at distance 1 from the step. We have checked that if detachment events into the upper terrace are also allowed (with the same rate of the detachments into the lower terrace), results do not change appreciably. The dynamics has been implemented via a rejection-free type of algorithm.

We have always kept fixed the deposition rate $F = 1$ and the diffusion coefficient $D = 5 \times 10^5$, so that the diffusion length is $\ell_D \approx 40$, as in Ref. The size of the system has been always $L = 1000$, large enough ($L \gg \Lambda_c$, see below) to allow for unstable mounds to form. We have varied $D'$, in order to change the ES length $\ell_{ES} = D/D' - 1$, and $R_d$.

B. The instability time

In order to analyze the breakdown of metastability, we focus first on the destabilization time $\tau_{ins}$, i.e., the time needed for the formation of the first critical nucleus. The identification of this object is not trivial and it has been discussed in Ref. Using the same numerical procedure for the identification of the nucleus, we have computed $\tau_{ins}$ for several values of the slope $m$, of the rate for thermal detachment $R_d$, and with varying $\ell_{ES}$.

The double-logarithmic plot of $\ln(\tau_{ins})$ vs $\ell_{ES}$ (Fig. 3) indicates a divergence as $\ell_{ES} \to 0$, with no clear-cut exponential or power-law behavior. Common (and intuitively expected) features are that increasing $m$ induces a delay in the destabilization process, just as, for fixed $m$, thermal detachment does.

More insight into how the destabilization process depends on $\ell_{ES}$ is obtained by considering the formation...
of the critical nucleus as the combination of two distinct processes. In the first place a dimer must be nucleated on a vicinal terrace. Then the dimer must grow up to a mound of a certain critical size that makes it unstable. The first event occurs at a rate $1/p_w$, strongly dependent on $\ell_{ES}$ but not on $L$. Hence we can write

$$\tau_{nucl}(L, \ell_{ES}) = \frac{1}{p_w(\ell_{ES})}.$$  \hspace{1cm} (10)

The value of $\tau_{nucl}$ can be written in its turn as $\tau_{dim}(\ell, \ell_{ES})/\ell$ where $\tau_{dim}$ is the time to nucleate a dimer on a vicinal terrace of size $\ell$ and $L/\ell$ is the number of such terraces: $\tau_{dim}$ could be computed analytically following Ref. 11, but it is straightforward to evaluate it numerically. Furthermore, an accurate determination of $\tau_{nucl}$ is important in order to evaluate correctly $1/p_w(\ell_{ES})$, which can be extracted by plotting $\tau_{nucl}/\tau_{dim}$ vs $\ell_{ES}$ (Fig. 4).

It turns out that, in almost all cases, $1/p_w$ diverges with $\ell_{ES} \to 0$ as $\exp(a/\sqrt{\ell_{ES}})$, with $a \approx 0.5$ and without evidence of a finite threshold. The only exception is the case of weaker slope, $m = 0.067$, where the divergence for small barrier is slower than exponential. This different behavior can be understood on the basis of the form of the unstable current $j_{ES}$ reported in Fig. 4. For $\ell_{ES} \leq 10$ the maximum $n_0$ of the current is very close to the slope $m = 0.067$ considered here. As a consequence, as the barrier is reduced the surface is more and more singular, rather than vicinal. The destabilization takes place because of a (weak) linear instability instead than through the breakdown of a metastable state. As a consequence the dependence of $1/p_w$ on $\ell_{ES}$ is not exponential, as for the other curves in Fig. 4. The divergence is a power-law, with an effective exponent 2.2 (see Fig. 4 inset), not far from the behavior $1/\ell_{ES}^2$ expected from the linear instability of a singular surface.

C. The mound width and its critical value

The evolution that, starting from a dimer nucleated on a vicinal terrace, leads to the formation of an unstable mound, is a very complicated process depending at each time on the detailed form of the profile. In order to understand it theoretically, one must focus on few parameters. The features that most naturally characterize a mound are its height $k$ and its width $\Lambda$. Both are useful in the analysis of the destabilization process. We first discuss the role of the mound width, which, despite being numerically harder to determine, it is conceptually more fundamental. In the following subsection we will consider the temporal evolution of the height, which is easily measured in simulations.

As discussed in Ref. 11, a good definition of the mound width is the size of the terrace immediately below the top one. For each value of $m, \ell_{ES}$ and $R_d$ it is thus possible to measure the critical width $\Lambda_c$, as the average width of mounds that start to diverge irreversibly. A plot of this quantity (Fig. 5) reveals the remarkable property that $\Lambda_c$ does not depend on $m$, nor on the rate of thermal detachment $R_d$. Moreover the dependence on the ES length is a power-law, with an effective exponent not far from 1/2. We now focus on the case without thermal detachment leaving for the next section the analysis of the effect of a finite $R_d$.

For the case without thermal detachment, the behavior displayed in Fig. 4 is naturally and consistently interpreted by relating the critical width $\Lambda_c(\ell_{ES})$ to the critical size $L_c(\ell_{ES})$ associated to the linear instability of
a singular surface

\[ \Lambda_c(\ell_{\text{ES}}) \propto L_c(\ell_{\text{ES}}). \tag{11} \]

This interpretation is further corroborated by a direct numerical evaluation of \( L_c(\ell_{\text{ES}}) \) as the smallest system size such that for a singular surface the instability can take place. The comparison of \( \Lambda_c \) with \( L_c(\ell_{\text{ES}}) \) (Fig. 5) strongly supports the validity of Eq. \( \text{(11)} \), confirming that a growing mound becomes unstable when its width is large enough to trigger the same type of instability at work for a singular surface. In this respect the width \( \Lambda \) is the fundamental quantity determining whether a mound is stable or unstable. Because of the difficulties in its numerical determination\( ^{11} \), it is not easy to analyze the detailed evolution of \( \Lambda \) in order to understand how the critical nucleus is generated by the dynamics. In particular, we aim at deriving a quantitative formula for the instability time \( \tau_{\text{inst}} \) or the relevant factor \( 1/p_u \). For this purpose it is more useful to study the mound height \( k \), which is easily measured in simulations.

D. Evolution of the mound height

The height is not as fundamental as the width for the determination of whether a mound is supercritical or not. For example a critical height cannot in principle be rigorously defined. This can be seen by taking a mound generated by the dynamics just a bit wider than \( \Lambda_c \) and strongly reducing its height: it remains supercritical. Nevertheless the dynamics couples the mound width and height so that the evolution of \( k \) typically reflects that of \( \Lambda \) and a height \( k_c \) of the critical nucleus can be in practice defined.

If a mound is described only in terms of its height, its dynamics is reduced to a one-dimensional random walk (RW), with only two possible processes for a mound of height \( k \): it may either become taller \((k \rightarrow k + 1)\) via dimer nucleation on its top terrace, or shorter \((k \rightarrow k - 1)\) if the bottom terrace delimiting the mound is filled. The increase (decrease) happens with probability \( p_+(k) \) \([1 - p_+(k)]\). It is possible to determine, via KMC simulations, the function \( p_+(k) \), which is reported in Fig. 6.

The stochastic nature of destabilization for large \( k \) is evident, consequence of the shape of \( p_+(k) \). For small \( k \), the probability that the mound grows is much smaller than \( 1/2 \). This implies that only rare events lead to mound growth. This effect is reduced as \( k \) is increased, up to a certain value \( k_c \), such that \( p_+(k) > 1/2 \) for \( k > k_c \). The threshold \( k_c \) plays the role of the effective height of the critical nucleus. The evolution is therefore biased toward the flat profile for \( k < k_c \) while the bias is toward higher \( k \) (destabilization) for \( k > k_c \). This translates into microscopic terms the metastable nature of a vicinal surface: it is stable with respect to small fluctuations, but unstable when a large fluctuation by chance appears. Fig. 7 shows that \( k_c \) grows as \( \ell_{\text{ES}} \) is reduced, invalidating the assumption of the argument in Sec. \( \text{II} \).

Using the values of \( p_+(k) \) extracted from the full KMC simulations, and taking them as the transition probabilities for an uncorrelated one-dimensional random walk, it is possible to compute \( 1/p_u \) as the fraction of times a walker starting in \( k = 1 \) reaches a large reference value (larger than \( k_c \), say 15) without touching the absorbing boundary \( k = 0 \). The results, presented in Fig. 7, agree very well with the outcome of simulations, indicating that, despite its rather crude simplifications, the random walk picture captures much of the destabilization process, and it allows to recover the dependence of the instability time \( \tau_{\text{inst}} \) on \( \ell_{\text{ES}} \). It is important to remark that this result is not at all trivial. Correlations in the random walk can generate, with the same transition probabilities \( p_+(k) \), very different values of \( 1/p_u \).

The agreement exhibited in Fig. 7 means that the uncorrelation of RW steps is a correct assumption. As it will be shown below, this is no more true when thermal detachment is allowed.

Within the RW picture it is also possible to derive analytically a formula for \( 1/p_u \). As shown in the Appendix one has to solve a stationary convection-diffusion equation with a space-dependent drift related to the form of \( p_+(k) \). By looking at Fig. 6 it is reasonable to take the explicit expression \( p_+(k) = p_0 e^{k/\ell_{\text{ES}}} \) for \( k < k_c \) and \( p_+(k) = p_{\text{max}} \) for \( k > k_c \), with \( p_0 e^{k_c} = p_{\text{max}} \). In this way we obtain (see the Appendix), in the limit \( k_c \gg 1 \)

\[ \frac{1}{p_u} = \left[ 1 + \frac{1}{p_{\text{max}} - 1} \right] e^{2k_c}. \tag{12} \]

The behavior of \( 1/p_u \) with decreasing \( \ell_{\text{ES}} \) is then due to a power-law divergence of the critical height \( k_c \). Since the height and the width of the critical nucleus scale in the same way\( ^{12} \), it is then possible to write \( 1/p_u \sim e^{a(m)\Lambda_c} \).
VI. THE EFFECT OF THERMAL DETACHMENT

We now analyze how the previous picture of the breakdown of the metastable state is modified by the possibility that atoms detach from steps or islands with rate \( R_d \). Figures 3, 4, and 5 show the effect of \( R_d \) on the instability time and on the critical width \( \Lambda_c \), respectively. At first sight these results might seem contradictory. While for \( R_d = 0 \) a dimer can split in two adatoms, which may diffuse and be incorporated by surrounding steps, restoring the situation with no dimer. This decay reduces the probability \( p_u^+(k) \) that a mound grows higher. A smaller \( p_u^+(k) \) clearly implies an increased \( 1/p_u \). Conversely, when a dimer splits during the growth of a high-symmetry surface, adatoms are not lost because there are no preexistent steps which capture them: hence such a splitting has no dramatic effect, leaving \( L_c \) (and hence on \( \Lambda_c \)) unchanged. This is the reason why switching \( R_d \) on is relevant for \( \tau_{\text{ins}} \) and not for \( \Lambda_c \).

The reduction of \( p_u^+(k) \) shown in Fig. 5 does not tell the whole story about the effect of thermal detachment. If we compare the value of \( 1/p_u \) determined numerically for the uncorrelated random walk with transition probabilities \( p_u^+(k) \) with the same quantity measured from the full KMC simulations (Fig. 7), we realize that the results do not agree and the mismatch grows with \( R_d \). The smaller \( p_u^+(k) \) is not enough to explain the instability time measured in KMC simulations: the assumption of uncorrelated steps is wrong when \( R_d \neq 0 \). The origin of the correlation is another subtle but relevant effect of the decay of dimers. When a dimer is formed on the top terrace of a mound (\( k \to k + 1 \)), owing to thermal detachment it is very easy that the dimer will soon decay so that \( k + 1 \) goes back \( k \). This increased chance that a splitting has no dramatic effect, leaving \( L_c \) (and hence on \( \Lambda_c \)) unchanged. This is the reason why switching \( R_d \) on is relevant for \( \tau_{\text{ins}} \) and not for \( \Lambda_c \).

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VII. CONCLUSIONS

In a nutshell, we have investigated the breakdown of the metastable step-flow for epitaxially grown vicinal sur-
faces. We have performed Kinetic Monte Carlo simulations showing that metastability holds for any strength of the ES barrier: the time needed for destabilization to occur diverges exponentially when the barrier goes to zero, both in the presence and in the absence of thermal detachment. Previous atomistic and continuum approaches to the problem do not reproduce this phenomenology. The crucial event determining the end of the metastable state is the formation, via a rare fluctuation, of a critical nucleus whose size diverges as the barrier goes to zero.

The dependence of the instability time on the parameters of the system can be summarized as

$$\tau_{\text{inst}}(L, m, \ell_{\text{ES}}, R_d) \approx \frac{\tau_{\text{dim}}(m, \ell_{\text{ES}}, R_d)}{(mL)} e^{[a(m,R_d)L_c(\ell_{\text{ES}})]},$$

(13)

where $\tau_{\text{dim}}$ is the time to nucleate a dimer on a vicinal terrace and $L_c(\ell_{\text{ES}})$ is the length associated to the linear instability on a singular surface. $\tau_{\text{dim}}$ has a well-known analytical form (at least for $R_d = 0$) and $L_c = \sqrt{\frac{K_{\text{ES}}}{\ell_{\text{ES}}}}$.

The only quantity which has not been determined is the prefactor $a$ in the exponent. The $\ell_{\text{ES}}$-dependence in $\tau_{\text{dim}}$ is weak and negligible for small $\ell_{\text{ES}}$.

The results presented fully clarify how the destabilization of step-flow comes about and also provide a semi-quantitative picture. The analytical interpretation would be completed by a direct computation of the probabilities $p_+(k)$ based on the microscopic dynamics. This remains a challenge for future work.

Another intriguing open question has to do with the difficulties of the continuum approach. In Sec. II we have shown that the minimal model with $J = K_{uu} \alpha + \alpha_{\text{ES}}(u)$ is completely unable to explain the phenomenology of the metastability process. A likely explanation for the failure of the continuum theory is that the current $J$ considered is too simple: it is well known that terms breaking the $z \rightarrow -z$ symmetry may be relevant, and a look at profiles from KMC simulations indicate that they play some role. These symmetry-breaking terms usually make the energy of motion nonderviable from a potential so that energetic arguments as those presented in Sec. II are not applicable. An analytical approach to the metastability of generalized Cahn-Hilliard equations with symmetry breaking terms is still to be found. But solving this problem may not be enough. Because of such additional terms, non-analytical regions could appear in the surface profile, in particular in the surroundings of minima where mounds merge. If this occurs a continuum approach may not be altogether applicable.

Despite these possible objections to the use of the minimal model it is important to remind that such a model is instead appropriate to describe at least qualitatively the linear and the nonlinear regimes of the destabilization of a singular surface. Why the model is not appropriate for the understanding the decay of the metastable regime is, in this light, a puzzle.

Finally, some considerations on two-dimensional systems. The argument given in Sec. II based on the hypothesis that critical mounds have constant height, can be easily extended to $d = 2$ and still provides a threshold. Within our approach, we can write the analogue of Eq. (10),

$$\tau_{\text{inst}}(L||, L\perp, \ell_{\text{ES}}) = \frac{\tau_{\text{dim}}(\ell)}{L\perp (L||/\ell)} p_n,$$

(14)

where $L||$ and $L\perp$ are the linear size of the system in the direction parallel and perpendicular to the slope, respectively. $\tau_{\text{dim}}(\ell)$ is the time to form a dimer on a terrace of size $\ell$ in the parallel direction per unit length in the perpendicular direction. Again, $p_n(\ell_{\text{ES}})$ is the probability that a dimer grows up to the critical size instead of being absorbed. Assuming that the form of the probabilities $p_+(k)$ will be similar to the one-dimensional case, it is reasonable to expect $1/p_n \sim \exp(k_s)$ also in this case. Since $k_s$ scales as $\Lambda_c$ in $d = 2$ as well, we conjecture that also in two dimensions the instability time diverges as $\exp(a/\ell^{1/2})$ when the ES barrier goes to zero.

**APPENDIX A: RANDOM WALK MODEL**

In this Appendix we compute analytically the probability $p_n$ that a freshly created dimer evolves into an unstable mound instead of being reabsorbed, given the probabilities $p_+(k) [1 - p_+(k)]$ of the process $k \rightarrow k + 1 [k \rightarrow k - 1]$. The problem is equivalent to the computation, for a random walk with absorbing boundaries in $0$ and $N \rightarrow \infty$, of the exit probability in $N$, with the walker starting initially in $k = 1$.

Let us call $\epsilon(x)$ the exit probability if the walker is deposited in $x$. This quantity obeys the recurrence relation

$$\epsilon(x) = p_+(x)\epsilon(x + 1) + (1 - p_+(x))\epsilon(x - 1),$$

(A1)

with boundary conditions $\epsilon(0) = 0$ and $\epsilon(N \rightarrow \infty) = 1$.

In the continuum limit

$$0 = a(x)\epsilon'(x) + \frac{1}{2}\epsilon''(x),$$

(A2)

with $a(x) = 2p_+(x) - 1$. Therefore we must solve a stationary convection-diffusion equation with space-dependent drift. The equation can be solved by separation of variables yielding

$$\epsilon(x) = C_1 + C_0 \int_0^x ds ' e^{-2f(s')},$$

(A3)

with $f(x') = \int_0^{x'} a(x'') dx''$.

To proceed further we specify the form of $p_+(k)$, in agreement with Fig. E

$$p_+(k) = \begin{cases} 
 p_0 e^k & k < k_c \\
 p_{\text{max}} & k > k_c 
\end{cases}$$

(A4)
with $p_0 e^{k_c} = p_{\max}$. Using this form we have, for $x < k_c$,
\begin{equation}
  f(x) \equiv f_1(x) = 2p_0 e^x - x, \quad (A5)
\end{equation}
so that, for $x < k_c$,
\begin{equation}
  \epsilon(x) \equiv \epsilon_1(x) = C_1 + C_0 \frac{(1 + 4p_0)e^{4p_0} - (1 + 4p_0 e^x)e^{-4p_0 e^x}}{16p_0^2}, \quad (A6)
\end{equation}
while for $x > k_c$
\begin{equation}
  \epsilon(x) \equiv \epsilon_2(x) = \epsilon_1(k_c) + C_0 \frac{e^{-2f_1(k_c)}}{2(2p_{\max} - 1)}. \quad (A7)
\end{equation}
The boundary condition $\epsilon(0) = 0$ sets $C_1 = 0$. The
second boundary condition determines the value of $C_0$
\begin{equation}
  \frac{1}{C_0} = \frac{(1 + 4p_0)e^{4p_0} - (1 + 4p_0 e^x)e^{-4p_0 e^x}}{16p_0^2} + \frac{e^{-2f_1(k_c)}}{2(2p_{\max} - 1)}. \quad (A8)
\end{equation}
The quantity we are interested in is $1/p_u = 1/\epsilon_1(x = 1)$. In the limit $k_c \gg 1$, which implies $p_0 \to 0$, and $e^{-2f_1(k_c)} \approx e^{2k_c}$, we find
\begin{equation}
  \frac{1}{p_u} = \left[ \frac{1}{e^2 - 1} \right] e^{2k_c}. \quad (A9)
\end{equation}