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Structure and Dynamics of Interfaces in the Epitaxial Growth and Erosion on (110) and (100) Crystal Surfaces

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Dissertation submitted to the Eberly College of Arts and Sciences
at West Virginia University
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in
Physics

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2004

ABSTRACT

Structure and Dynamics of Interfaces in the Epitaxial Growth and Erosion on (110) and (100) Crystal Surfaces

Artem Levandovsky

We present unified theory of the far-from-equilibrium interfacial phenomena occurring in the multilayer homoepitaxial growth and erosion on (110) and (100) crystal surfaces. Within a unified model, here we elucidate the multitude of novel states on (110) and (100) surfaces as well as the transitions between them. In particular, by analytic arguments and numerical simulations, we address experimentally observed transitions between two types of rippled states on (110) surfaces. We discuss several intermediary interface states intervening, via consecutive transitions, between the two rippled states. One of the intermediary interface states, the Rhomboidal Pyramid State, was theoretically anticipated by us and subsequently seen by de Mongeot and coworkers in the epitaxial erosion of Cu(110) and Rh(110) surfaces. In addition, we find a number of interesting intermediary states having structural properties somewhere between those of rippled and pyramidal states. Prominent among them are the Rectangular Rippled states of long roof-like objects (huts) recently seen on Ag(110) surface. Also, we predict existence of striking interfacial structures that, unusually, carry persistent surface currents. These so called Buckled Rippled interface states are far-from-equilibrium relatives of the Abrikosov vortex state in type-II superconductors. We discuss the mechanisms of the coarsening growth of the multitude of the interfacial states on (110) crystal surfaces. The coarsening of the common rippled states on (110) surfaces is shown to be mediated by ensembles of climbing dislocations destroying perfect periodic order (coherence) of these growing structures. We also discuss the experimentally observed enhanced coarsening of the Rhomboidal Pyramid state intervening between the two rippled states. Finally, the general phenomenology of multilayer epitaxial growth and erosion on square (001) symmetry crystal surfaces and elucidate recently observed 45 degree rotation transition between pyramidal states on (110) surfaces. We predict and characterize novel intermediary states of many-sided pyramids ubiquitously intervening in these transitions and causing an enhanced roughening. We elucidate the actual effect of the vertical (pyramid-pit) growth asymmetry on the multitude of states on (100) and (110) crystal surfaces.

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Chapter 1

INTRODUCTION

Depositions of thin films on crystalline substrates is very significant for modern technologies. One of the most promising techniques to grow thin films is the Molecular Beam Epitaxy (MBE) that was originally developed as a method to obtain atomically flat thin films [1]. However, numerous experiments show that the resulting film interfaces are often not flat.

The dynamics of crystal interfaces during epitaxial growth reflects a delicate competition between the molecular flux and the relaxation of the surface profile through surface diffusion of adatoms. Particularly important are adatom interactions with steps on the crystal surface. These steps are characterized by energy barriers that hinder the movement of atoms between layers of the growing interface. These are so called Ehrlich-Schwoebel-Villain energy barriers [2-4]. These barriers lead to a surface current of adatoms towards the upper step edge (“up-hill” surface current). Such a current yields an instability of a flat crystal surface which triggers the formation of fascinating structures such as mounds and pyramids developing across the growing interface [5], [6]. By studying the diffusive motion of adatoms on vicinal surfaces with step edge barriers one indeed finds [4] that the surface nonequilibrium current J^{NE} is really an up-hill current. Consequently, it tends to increase the local interface slope, i.e., destabilize flat crystals

surfaces. However, for sufficiently large slopes there are other processes that counterbalance the destabilizing effect, so that the net current in the *nonequilibrium* situation vanishes for certain slopes (slope selection). Transient mobility effects, such as funneling and knockout processes [7,8] can lead to zeros of $J^{\text{NE}}(M)$ even for small values of the interface slope M [9,10]. Due to the slope selection, the interface breaks up into structures, such as pyramid-like mounds. Usually, slopes of pyramid facets correspond to stable zeros of the surface current. Over the past decade it has become clear that the interface of films grown by MBE indeed often exhibit the formation of pyramids or pyramid-like structures, even in the case of homoepitaxial crystal growth. These structures have been seen in many experiments, e.g., for homoepitaxy of GaAs [6,11], Cu [5], Ge [12] and Fe [13,14], all grown on singular (001) substrates, as well as for homoepitaxy of Rh [15] and Pt [16] on the (111) surface. The experiments show that the lateral size λ and the height w of these mounds both grow in time as power laws with the same exponent. Thus, the ratio w/λ corresponding to the pyramid slope, approaches a constant value at long times. Therefore, there is a slope selection in a typical MBE growth. The corresponding coarsening exponents, for the growth of λ and w , were found from experiments to depend on the symmetry of the surface. For example, for the growth on (001) surfaces the experimental value of the coarsening exponent is close to 1/4, whereas for the growth on (111) surfaces the exponent reported is 1/3 [15]. To explain these findings, Moldovan and Golubovic [19] have introduced kinetic scaling theory which provided for the first time an analytic understanding of the coarsening laws observed in the experiments and simulations of the MBE growth. Their theory has been motivated in part by recent theories of phase ordering processes such as the growth of

domains in magnetic systems [17]. Moldovan and Golubovic investigated continuum models for various types of the crystal surface symmetry. Their study of the growth on the *isotropic* and *hexagonal* (111) symmetry surfaces shows that the interface is characterized by the presence of a single characteristic length scale $\lambda(t)$ = pyramid size that grows in time as a power law, $\lambda(t) \sim t^{n_c}$, with the coarsening exponent $n_c = 1/3$. This value was related to the fact the major coarsening mechanism on isotropic and hexagonal (111) surfaces is local pyramid coalescence.

In contrast to (111) crystal surfaces, in the growth on square (001) symmetry surfaces, the pyramids arrange into nearly perfectly periodic square lattices [18, 19]. This is best documented by looking at the network of pyramid *edges* (lines along which pyramid facets meet), which form here a nearly regular square lattice. Moldovan and Golubovic [19] found that the perfect periodic order of this edge lattice is disrupted by occasional presence of defects that are characterized as the *dislocations* of the edge network. These dislocations represent topological defects of otherwise almost perfect square lattice of pyramid edges. The most important finding of Moldovan and Golubovic is that the interface coarsening proceeds by the *motion* of these dislocations that can be characterized as the dislocation climb [19]. The dislocations of edge lattices are thus crucial for the interfacial coarsening of the square symmetry (001) surfaces. Interestingly, the presence of dislocations causes a multi-scaling behavior of the interfacial morphology and coarsening, i.e., the existence of several long length-scales that grow in time with different exponents. One of them is the lateral pyramid size $\lambda(t)$ that grows as $\lambda(t) \sim t^{n_c}$, with the coarsening exponent $n_c \cong 0.25$. Other length scales are related to the presence of dislocations. They grow much faster than $\lambda(t)$. Thus, the distance between dislocations

in the same row of the edge lattice, $\xi(t)$, grows as $\xi(t) \sim t^{n_\xi}$. From their simulations, Moldovan and Golubovic found that $n_\xi \cong 0.5$ [19]. Also, they developed a kinetic scaling theory that analytically explained the experimentally found coarsening exponents for the MBE growth on the square symmetry (001) surfaces.

This thesis is all devoted to the theoretical elucidation of the most recent experimental discoveries in the area of the epitaxial growth and erosion of crystal surfaced. Here, we provide a theoretical framework for understanding several important experimental findings that emerged in this area over the past four years. Thus, in Chapters 2 and 3 of this thesis, we present unified theory of the far from equilibrium interfacial phenomena occurring in the multilayer homoepitaxial growth and erosion on the *low-symmetry* (110) crystal surfaces. As evidenced by recent experiments [20-22], these *rectangular* symmetry surfaces exhibit a multitude of interesting non-equilibrium interfacial structures, such as the *rippled* one-dimensionally periodic states that are not present in the homoepitaxial growth and erosion on the high symmetry (100) and (111) crystal surfaces discussed in the previous theoretical works, such as aforementioned theory of Moldovan and Golubovic [19]. Within a unified model, here we elucidate the multitude of these novel states on (110) surfaces as well as the kinetic phase transitions between them. In particular, by analytic arguments and numerical simulations, we address the experimentally observed transitions between two types of rippled states on (110) surfaces, with their wave vectors along the two principal axis of (110) surface [20, 21, 24]. We discuss several interesting intermediary interface states that intervene, via consecutive transitions, between the two rippled states. One of them is the Rhomboidal Pyramid State, theoretically anticipated in our paper [23] and subsequently seen by de

Mongeot and coworkers [24], in the epitaxial erosion of Cu(110) and Rh(110) surfaces. In addition, we find a number of interesting intermediary states having structural properties somewhere between those of rippled and pyramidal states. Prominent among them are the Rectangular Rippled states of long roof-like objects (huts) recently seen on Ag(110) surface [25]. Also, we predict the existence of striking interfacial structures that, unusually, carry persistent surface currents of ad-atoms. These, here called Buckled Rippled interface states, are far-from-equilibrium relatives of the Abrikosov vortex state in type-II superconductors. We discuss the mechanisms of the coarsening growth of the multitude of the interfacial states on (110) crystal surfaces. The coarsening of the common rippled states on (110) surfaces is shown here to be mediated by ensembles of climbing dislocations destroying perfect periodic order (coherence) of these growing structures. We also discuss the experimentally observed enhanced coarsening of the Rhomboidal Pyramid state intervening between the two rippled states [24].

In Chapter 4 of this thesis, we address the general phenomenology of the multilayer epitaxial growth and erosion on square symmetry (001) crystal surfaces. Our study is directly motivated by the very recently experimentally observed 45-degree rotation transitions between pyramidal states on Ag(001) surfaces [26]. Here and in Ref. [27], we elucidate this phenomenon by means of a unified model for the growth and erosion on (001) surfaces. For the first time, we predict and characterize several novel interface states of many-sided pyramids intervening in these transitions. Common signature of these intervening states is an enhanced roughening. We use our model to discuss the coarsening dynamics of the multitude of interface states on (001) crystal surfaces, and reveal the real role of previously elusive vertical (pyramid-pit) asymmetry.

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Chapter 2

DISLOCATION DYNAMICS AND COARSENING OF RIPPLED STATES ON (110) SURFACES INTERFACIAL STATES AND FAR-FROM- EQUILIBRIUM TRANSITIONS IN THE EPITAXIAL GROWTH AND EROSION ON (110) CRYSTAL SURFACES

I. INTRODUCTION

Multilayer epitaxial growth and erosion of crystal surfaces often exhibits the formation of fascinating surface nanostructures, [1-10]. At their origin is the classical Ehrlich-Schwoebel-Villain instability, [5,6]. Thus, on high symmetry (100) and (111) crystal surfaces, pyramidal structures are frequently seen both in the homoepitaxial deposition growth and in erosion, which is essentially a deposition of surface vacancies by ion beams, [7]. These pyramids grow in time via coarsening processes that dominate the far from equilibrium dynamics of crystal interfaces. These phenomena were studied

in numerous experiments and simulations on high symmetry crystal surfaces, such as the square symmetry (100) surfaces and the hexagonal symmetry (111) crystal surfaces, [1-4,7,8,12]. On the other hand, much less is known about related growth phenomena on *low symmetry* surfaces. Thus, the far from equilibrium interfacial structures formed in the epitaxial growth and erosion on rather typical *rectangular* symmetry (110) crystal surfaces have attracted attention only recently, [9,10]. Rather than pyramids, rippled one-dimensionally (nearly) periodic structures are more commonly seen on these crystal surfaces, such as Fe(110) [11], Ag(110) [9,10], Cu(110) and Rh(110) [13]. There are two types of these rippled states, with their wave-vectors oriented along the two perpendicular principal axes of the (110) surfaces. In addition to the rippled states, intriguing *intermediary states* of interface have been recently revealed in the "90-degrees ripple rotation" transitions between the two types of rippled states on Ag (110) surfaces [9,10], and, more recently, on Cu(110) and Rh(110) surfaces [13]. These intermediary states are believed to have a pyramidal character. Most recently, striking pyramidal structures have been seen also on Al(110), having the form of self-assembled "huts", i.e., roof-like pyramids [14].

Here, we discuss these far from equilibrium phenomena occurring in the multilayer epitaxial growth and erosion on (110) surfaces. In this Chapter, we present detailed exposition of the theory briefly outlined before in our letter [3]. We elucidate theoretically the non-equilibrium interfacial structures growing on these low symmetry crystal surfaces. As evidenced by experiments, the rectangular symmetry (110) surfaces exhibit a multitude of interesting non-equilibrium interfacial structures that are not present in the extensively studied homoepitaxial growth and erosion on the high

symmetry (100) and (111) crystal surfaces. Within a unified model, our study exposes generic multitude of novel interfacial states on (110) surfaces as well as the far from equilibrium phase transitions between these states (Sec. II). By analytic arguments and numerical simulations, we investigate in detail the generic non-equilibrium phase diagram of these surfaces. In particular, we address the experimentally observed transitions and intermediary states between the two aforementioned types of rippled states on (110) surfaces. We predict and discuss a number of intermediary interface states intervening, via consecutive transitions, between the two rippled states (Secs. III and IV). One of them is the Rhomboidal Pyramid State that has been theoretically predicted by us in [3] and subsequently seen by de Mongeot and coworkers in the epitaxial erosion of Cu(110) and Rh(110) surfaces [13]. In addition, our model yields a number of experimentally interesting intermediary states having structural properties somewhere between those of rippled and pyramidal states (Secs. III and IV). Among them are two Rectangular Rippled states of long roof like objects (huts). This state, theoretically anticipated by us in [3], most likely represents the long times form of the aforementioned roof-like pyramid (huts) state, more recently revealed to emerge in the epitaxial growth on Al(110) surface [14]. We predict these huts to merge into fascinating interfacial structures, the Rectangular Rippled states, in which the roof-like pyramids self-assemble into novel kinds of rippled states. In fact, our basic Rectangular Rippled structure, the checkerboard arrangements of huts and pits (inverted huts), has been clearly seen in the erosion experiments on Ag(110) [see Ref. 10, Fig. 4(d)]. We predict that there are two types of the Rectangular Rippled states, with their wave-vectors oriented along the two perpendicular principal axes of the (110) surfaces. To elucidate the non-equilibrium

phase transition between these states, we introduce a nontrivial generalization of the classical Gibbs phase coexistence rule to the situations involving far-from-equilibrium phase transitions [Secs. III and IV, and the Appendix B]. Our theory [3] has revealed also the striking Buckled Rippled interface state, discussed here in detail. Unusual feature of this state is that it exhibits an interfacial structure that carries *persistent surface currents of ad-atoms* (Sec. IV). The Buckled Rippled state is thus a far-from-equilibrium relative of the Abrikosov vortex state in type-II superconductors. In the Buckled Rippled state however the role of the superconducting persistent electric currents is played by the persistent surface currents, i.e., the mass currents transporting ad-atoms across the growing interface.

In this study, we predict also the coarsening laws of the dynamics of common rippled and other far from equilibrium states on (110) crystal surfaces. We discuss mechanisms of the coarsening process of various interfacial states on these simplest low symmetry crystal surfaces (Sec. IV). The coarsening, i.e., the growth of the spatial period of the rippled states on (110) surfaces is shown to be mediated by ensembles of climbing dislocations. Like to the dislocations of equilibrium two-dimensional smectic A liquid crystals [15], the dislocations here destroy perfect periodic order of the growing rippled structures. In the presently studied far-from-equilibrium systems, however, these topological defects have a prominent dynamical character. As discussed in Sec. IV, the growth of the rippled states structural length scales is directly related to the motion and annihilations of these dislocations. In Sec. IV we also discuss the interfacial phenomena underlying the experimentally observed enhanced coarsening of the Rhomboidal Pyramid state intervening between the two Rippled states [13].

This Chapter is organized as follows: In Sec. II, we derive our unified phenomenological model for multilayer epitaxial growth and erosion on (110) surfaces. In the following sections, we analyze the model by a combination of analytic arguments and numerical simulations: In Sec. III, we derive the kinetic phase diagram of the model exhibiting generic multitude of growing interfacial states on (110) surfaces. In Sec. IV, we discuss the structure and coarsening dynamics of these states, as well as the experiments on Cu(110) and Rh(110) surfaces. In Sec. V, we analyze the effect of *Vertical Anisotropy* on surface morphology. Appendix A outlines facet stability analysis significant for the overall understanding of the kinetic phase diagram. Appendix B discusses a nontrivial generalization of the classical Gibbs phase coexistence rule to the situations involving far-from-equilibrium phase transitions. Our generalization is essential for understanding of the transition between two types of growing Rectangular Rippled states on (110) crystal surfaces.

II. RECTANGULAR SYMMETRY AND INTERFACE DYNAMICS

In this section, we introduce a continuum model for the epitaxial growth and erosion on (110) crystal surfaces. We base our discussion on the general phenomenological approach to multilayer epitaxial growth in the absence of (typically weak) adatom adsorptions and vacancy creation [5, 6]. Under these conditions the deposited film volume is conserved and the height function $h(\vec{x}, t)$ describing interface shape must obey this conservation law. In the frame co-moving with the interface, the interface velocity $\frac{\partial h}{\partial t}$ can be thus represented as a divergence of the surface current

$$\vec{J} = (J_1, J_2),$$

$$\frac{\partial h(\vec{x}, t)}{\partial t} = -\vec{\nabla} \cdot \vec{J} = -\frac{\partial J_1}{\partial x_1} - \frac{\partial J_2}{\partial x_2}. \quad (2.1)$$

Here $\vec{x} = (x_1, x_2)$ is two-dimensional base plane vector, see Fig. 1(a). Due to the vertical translation symmetry $h \rightarrow h + \text{const}$, the surface current can depend only on spatial derivatives of $h(x_1, x_2, t)$. It is convenient to express $\vec{J}$ in the form

$$\vec{J} = \vec{J}^{NE}(\vec{\nabla}h) + \vec{J}^{curv}. \quad (2.2)$$

Here, the first term is the surface nonequilibrium current $\vec{J}^{NE}(\vec{M})$ which is a function of the local interface slope vector $\vec{M} = \vec{\nabla}h = (M_1, M_2)$ only, see Fig. 1(b). $\vec{J}^{curv}$ in Eq. (2.2) is the surface curvature current. This current depends on higher order spatial derivatives of h and vanishes on a flat surface (facet). For example, for an isotropic surface, $\vec{J}^{curv}$

Fig. 1. (a) The interface growth process. (b) Surface nonequilibrium current $\vec{J}^{NE}(\vec{M})$ as the function of the local interface slope vector $\vec{M}$. (c) Transformations of the surface nonequilibrium current vector under the symmetry transformations of the (110) surface. (d) The absence of the diagonal reflection symmetry on (110) surfaces: The slope vectors $\vec{M}$ and $\vec{M}'$ here are related by diagonal reflection. However, the corresponding current vectors $\vec{J}^{NE}(\vec{M})$ and $\vec{J}^{NE}(\vec{M}')$ are *not* related by the diagonal reflection.

contains a term isomorphic to the Mullins surface diffusion current $\propto -\vec{\nabla}(\nabla^2 h)$ contributing to the interface velocity in Eq. (2.1) the term $-\kappa(\nabla^2)^2 h$. For the rectangular symmetry surfaces, this contribution to Eq. (2.1) has the more general form

$$-\vec{\nabla}\vec{J}^{sd} = -\kappa_{11}\left(\frac{\partial}{\partial x_1}\right)^4 h - 2\kappa_{12}\left(\frac{\partial}{\partial x_1}\right)^2\left(\frac{\partial}{\partial x_2}\right)^2 h - \kappa_{22}\left(\frac{\partial}{\partial x_2}\right)^4 h \quad (2.3)$$

Note that for isotropic surfaces, $\kappa_{11} = \kappa_{12} = \kappa_{22} = \kappa$, whereas for square symmetry (001) surfaces, $\kappa_{11} = \kappa_{22} \neq \kappa_{12}$.

The (110) surface has rectangular symmetry, and the natural coordinate system (x_1, x_2) with principal axes along the sides of the surface rectangular unit cell. This coordinate system is already assumed in Eq. (2.3) above, as well as in the following discussions. Rectangular symmetry of (110) involves two major symmetry operations, which are the reflections across the principal axis of (110) - the reflection

$\mathfrak{R}_1 : (x_1, x_2) \rightarrow (-x_1, x_2)$, and the reflection $\mathfrak{R}_2 : (x_1, x_2) \rightarrow (x_1, -x_2)$. As $M_1 = \frac{\partial h}{\partial x_1}$ and

$M_2 = \frac{\partial h}{\partial x_2}$, under $\mathfrak{R}_1$,

$$\mathfrak{R}_1 : (M_1, M_2) \rightarrow (-M_1, M_2), \quad (2.4)$$

while under $\mathfrak{R}_2$,

$$\mathfrak{R}_2 : (M_1, M_2) \rightarrow (M_1, -M_2). \quad (2.5)$$

The rectangular symmetry of (110) imposes a few ubiquitous properties of the non-equilibrium current $\vec{J}^{NE}(\vec{\nabla}h)$. The current vector

$$\vec{J}^{NE}(\vec{M}) = (J_1(M_1, M_2), J_1(M_1, M_2)),$$

must transform in the same way the slope vector $\vec{M} = \vec{\nabla}h = (M_1, M_2)$ transforms under symmetry transformations leaving the rectangle, i.e., the (110) surface invariant. In other words, for any surface symmetry operation S

$$\vec{J}^{NE}(S \vec{M}) = S \vec{J}^{NE}(\vec{M}), \quad (2.6)$$

see Fig. 1(c). Thus, under $\mathfrak{R}_1$,

$$\begin{aligned} J_1^{NE}(-M_1, M_2) &= -J_1^{NE}(M_1, M_2), \\ J_2^{NE}(-M_1, M_2) &= J_2^{NE}(M_1, M_2), \end{aligned} \quad (2.7)$$

while under $\mathfrak{R}_2$, by Eq. (2.5),

$$\begin{aligned} J_1^{NE}(M_1, -M_2) &= J_1^{NE}(M_1, M_2), \\ J_2^{NE}(M_1, -M_2) &= -J_2^{NE}(M_1, M_2). \end{aligned} \quad (2.8)$$

Likewise, under the inversion symmetry of (110), $\text{Inv} = \mathfrak{R}_1 \otimes \mathfrak{R}_2$, one has $\text{Inv}: (x_1, x_2) \rightarrow (-x_1, -x_2)$; thus $\text{Inv}: (M_1, M_2) \rightarrow (-M_1, -M_2)$. Thus, the inversion symmetry implies

$$\vec{J}^{NE}(-\vec{M}) = -\vec{J}^{NE}(\vec{M}). \quad (2.9)$$

We stress that the rectangular symmetry (110) surfaces do *not* have invariance under the diagonal reflection, $\mathfrak{R}_{diag}: (x_1, x_2) \rightarrow (x_2, x_1)$, i.e. $(M_1, M_2) \rightarrow (M_2, M_1)$. Thus, on rectangular symmetry surfaces, in general,

$$\vec{J}^{NE}(M_1, M_2) \neq \vec{J}^{NE}(M_2, M_1), \quad (2.10)$$

simply because the principal axis of (110) are *not* equivalent to each other, see Fig 1(d). In this respect, (110) surfaces are different from the square symmetry (001) surfaces for which Eq. (2.10) holds with equality [1,2,4].

Commonly, stable zeros of the non-equilibrium current, solving the equation $\vec{J}^{NE}(\vec{M}) = \vec{0}$, correspond to the preferred slopes $\vec{M}$ of the facets that develop across the growing interface and organize into large structures, e.g., the square pyramids on (100) surfaces, [1-4]. Importantly, by Eq. (2.6), if $\vec{M}$ is a zero of $\vec{J}^{NE}$, then $S \vec{M}$ is also a zero of $\vec{J}^{NE}$, where S is any surface symmetry operation. For (110) surfaces, $S = (\mathfrak{R}_1, \mathfrak{R}_2, \text{Inv})$ and one can see that there are *three* possible types of these preferred slope vectors:

(i) *Singlet*, for which *both* slope components vanish, $M_1=M_2=0$, see Fig 2(a).

(ii) *Doublets* of two equivalent (symmetry related) slope vectors, for which *one* of the two components of the slope vector vanishes. There are two types of doublets: the pair $(\pm M_1, 0)$, and the pair $(0, \pm M_2)$, called, respectively, as R_1 - and R_2 -doublet in Fig. 2(b). Importantly for the following, these two types of doublets are *not* equivalent, to each other. The diagonal reflection, R_{diag} , that would relate them is not a symmetry of (110) surface, as noted in Eq. (2.10) above.

(iii) *Quartet* of four equivalent slope vectors, for which *none* of the slope components vanishes: $(\pm M_1, \pm M_2)$, see Fig 2(c).

In the unstable epitaxial growth, the singlet at $\vec{M} = 0$ is unstable, and stable facets may thus correspond to the doublets in Fig. 2(b) or to the quartet in Fig. 2(c). In Secs. III

Fig. 2. Types of zeros of the surface nonequilibrium current on (110) surfaces: (a) singlet, (b) two types of doublets, and (c) quartet.

and IV, we will see that the stable doublet $(\pm M_1, 0)$ gives rise to the structure of alternating facets, with the slopes $(\pm M_1, 0)$, comprising the rippled state periodic along the x_1 -direction, the R_1 state. Likewise, the stable doublet $(0, \pm M_2)$ gives rise to the rippled state R_2 periodic along the x_2 -direction. On the other side, the stable *quartet* $(\pm M_1, \pm M_2)$ is shown in Secs. III and IV to give rise to *two-dimensionally* periodic interface structures of four-sided pyramid like objects, the Rhomboidal Pyramid state.

We will expose the phenomenology of the epitaxial growth and erosion on (110) surfaces, by considering the dynamical model Eq. (2.1) with generic form of the non-equilibrium current $\vec{J}^{NE}(\vec{M})$. This current can be represented as an expansion in powers of $\vec{M}$ respecting the stringent restrictions imposed by the rectangular symmetry. Thus, by the inversion symmetry of (110) in Eq. (2.9), this expansion must contain only odd powers of $\vec{M}$. Furthermore, by respecting the rectangle reflection symmetries in Eqs. (2.7) and (2.8), we arrive at the general expansion of the form

$$\begin{aligned} J_1^{NE}(M_1, M_2) &= M_1[r_1 - u_{11}M_1^2 - u_{12}M_2^2 + \dots], \\ J_2^{NE}(M_1, M_2) &= M_2[r_2 - u_{22}M_2^2 - u_{21}M_1^2 + \dots]. \end{aligned} \quad (2.11)$$

By considering typical situations with small selected slopes, the simplest basic model is naturally obtained by truncating out the higher order terms in the ellipses in Eq. (2.11). In this limit, one is led to model the $\mathcal{J}^{curv}$ term in Eq. (2.2) by the anisotropic version of the surface diffusion current. As discussed before, it contributes to the local interface velocity the term exhibited in Eq. (2.3). We stress that in the expression for the non-equilibrium current, Eq. (2.11), $r_1 \neq r_2$, $u_{12} \neq u_{21}$, and $u_{11} \neq u_{22}$ for general (110) surfaces, as a consequence of the diagonal asymmetry, Eq. (2.10). This is in contrast to the square

symmetry (100) surfaces that have diagonal symmetry $\vec{J}^{NE}(M_1, M_2) = \vec{J}^{NE}(M_2, M_1)$,
implying $r_1 = r_2$, $u_{12} = u_{21}$, and $u_{11} = u_{22}$.

For the special case $u_{12} = u_{21} = u$, the non-equilibrium current in Eq. (2.11) becomes a gradient of a potential,

$$\vec{J}^{NE} = - \frac{\partial U(\vec{M})}{\partial \vec{M}}. \quad (2.12a)$$

For the case $u_{12}=u_{21}=u$, the potential

$$U(M) = -\frac{r_1}{2}M_1^2 - \frac{r_2}{2}M_2^2 + \frac{u_{11}}{4}M_1^4 + \frac{u}{2}M_1^2M_2^2 + \frac{u_{22}}{4}M_2^4, \quad (2.12b)$$

generates, by Eq. (2.12a), the current in Eq. (2.11), and the interface dynamics equation (2.1) can be shown to be equivalent to

$$\frac{\partial h(x, t)}{\partial t} = - \frac{\delta F_{eff}}{\delta h(x, t)}. \quad (2.13a)$$

Here, F_{eff} is an effective free energy functional of the form $F_{eff}(h) = F_{sd} + F_{NE}$, with

$$F_{NE} = \int d^2x \ U(\vec{M}) \quad (2.13b)$$

and

$$F_{sd} = \int d^2x \left[\frac{\kappa_{11}}{2} \left(\frac{\partial^2 h}{\partial x_1^2} \right)^2 + \frac{\kappa_{12}}{2} \left(\frac{\partial^2 h}{\partial x_1 \partial x_2} \right)^2 + \frac{\kappa_{22}}{2} \left(\frac{\partial^2 h}{\partial x_2^2} \right)^2 \right]. \quad (2.13c)$$

We stress that for $u_{12} \neq u_{21}$ there is *no* effective free energy that would generate dynamics in the form as in Eq. (2.13a). In the following we will discuss, both analytically and numerically, the general case with $u_{12} \neq u_{21}$. This inequality turns out to be essential

for the existence of a novel interface state, the Buckled Rippled state (see Secs. III and IV). This state is prohibited in the case with $u_{12} = u_{21}$ when the effective free energy exists.

By Eqs. (2.1), (2.2), (2.3), and (2.11), we obtain the full model

$$\begin{aligned}
\frac{\partial h}{\partial t} = & -\frac{\partial}{\partial x_1} \left\{ \frac{\partial h}{\partial x_1} \left[r_1 - u_{11} \left(\frac{\partial h}{\partial x_1} \right)^2 - u_{12} \left(\frac{\partial h}{\partial x_2} \right)^2 \right] \right\} \\
& -\frac{\partial}{\partial x_2} \left\{ \frac{\partial h}{\partial x_2} \left[r_2 - u_{22} \left(\frac{\partial h}{\partial x_2} \right)^2 - u_{21} \left(\frac{\partial h}{\partial x_1} \right)^2 \right] \right\} \\
& -\kappa_{11} \left(\frac{\partial}{\partial x_1} \right)^4 h - 2\kappa_{12} \left(\frac{\partial}{\partial x_1} \right)^2 \left(\frac{\partial}{\partial x_2} \right)^2 h - \kappa_{22} \left(\frac{\partial}{\partial x_2} \right)^4 h .
\end{aligned} \tag{2.14}$$

The model in Eq. (2.14) depends on six major parameters of the nonequilibrium current $\vec{J}^{NE}(\vec{M})$ Eq. (2.10), that are r_1 , r_2 , u_{11} , u_{22} , u_{12} , and u_{21} . Importantly, this number can be reduced to only *three* independent parameters. This reduction is achieved by applying to the model in Eq. (2.14) the *anisotropic* rescaling:

$$h = Hh', \quad x_1 = X_1 x'_1, \quad x_2 = X_2 x'_2, \quad t = T t', \tag{2.15}$$

with suitably chosen the rescaling coefficients H , T , X_1 , and X_2 . By choosing them as

$$\begin{aligned}
H = T = & \frac{1}{4} \left(\frac{r_1}{\sqrt{u_{11}}} + \frac{r_2}{\sqrt{u_{22}}} \right)^2, \\
X_1 = & H^{3/4} u_{11}^{1/4}, \quad X_2 = H^{3/4} u_{22}^{1/4},
\end{aligned} \tag{2.16}$$

the model in Eq. (2.14) assumes the form:

$$\begin{aligned} \frac{\partial h'}{\partial t'} = & -\frac{\partial}{\partial x'_1} J'_1 - \frac{\partial}{\partial x'_2} J'_2 \\ & -k_{11} \left(\frac{\partial}{\partial x'_1} \right)^4 h' - 2k_{12} \left(\frac{\partial}{\partial x'_1} \right)^2 \left(\frac{\partial}{\partial x'_2} \right)^2 h' - k_{22} \left(\frac{\partial}{\partial x'_2} \right)^4 h' , \end{aligned} \quad (2.17a)$$

with

$$\begin{aligned} J'_1 &= M'_1 \left[1 + a - M_1'^2 - (b+c)M_2'^2 \right] , \\ J'_2 &= M'_2 \left[1 - a - M_2'^2 - (b-c)M_1'^2 \right] . \end{aligned} \quad (2.17b)$$

Here, $M'_1 = \frac{\partial h'}{\partial x'_1}$ and $M'_2 = \frac{\partial h'}{\partial x'_2}$, whereas a , b , and c are the three independent

dimensionless parameters:

$$\begin{aligned} a &= \frac{r_1/\sqrt{u_{11}} - r_2/\sqrt{u_{22}}}{r_1/\sqrt{u_{11}} + r_2/\sqrt{u_{22}}} , \\ b &= \frac{u_{12} + u_{21}}{2\sqrt{u_{11}u_{22}}} , \quad c = \frac{u_{12} - u_{21}}{2\sqrt{u_{11}u_{22}}} , \end{aligned} \quad (2.18)$$

and $k_{11} = \frac{H}{X_1^4} \kappa_{11}$, $k_{12} = \frac{H}{X_1^2 X_2^2} \kappa_{12}$, and $k_{22} = \frac{H}{X_2^4} \kappa_{22}$. By comparing Eq. (2.11) and Eq.

(2.17b), one can see that the effect of the anisotropic rescaling Eq. (2.15) is to replace u_{11} and u_{22} by unity, whereas r_1 and r_2 are replaced by $1+a$ and $1-a$ respectively, while u_{12} and u_{21} are replaced by $b+c$ and $b-c$ respectively. We stress that the polar angles of the slope vectors $\vec{M} = (M_1, M_2) = |\vec{M}|(\cos \theta, \sin \theta)$ of the original and the rescaled model are related by

$$\tan(\theta) = \left(\frac{u_{22}}{u_{11}} \right)^{1/4} \tan(\theta') , \quad (2.19)$$

as can be shown by Eqs. (2.15) and (2.16), by noting that $\tan(\theta) = M_2/M_1$ and $\tan(\theta') = M'_2/M'_1$. Also, we recall that for the square symmetry surfaces, $r_1 = r_2$, $u_{12} = u_{21}$, and $u_{11} = u_{22}$, so, for them, by Eqs. (2.18), $a = 0$ and $c = 0$. For this square symmetry case, the model Eq. (2.16) reduces to the model discussed by Siegert [2], and Moldovan and Golubovic [1]. Finally, we note that for the case $u_{12} = u_{21}$, one has $c = 0$ by Eq. (2.18). In this case, the model Eq. (2.17) can be written in the form Eq. (2.13) employing the effective free energy.

III. KINETIC PHASE DIAGRAM

The model in Eq. (2.17) exhibits a number of interfacial states generic for (110) crystal surfaces, as documented in its (far-from-equilibrium) phase diagram in Figs. 3 and 4. The phase diagram is deduced by linear stability analysis of the facets corresponding to the zeros of the non-equilibrium current $\vec{J}^{NE}(\vec{M})$ in Eq. (2.17b), and further corroborated by numerical simulations of the model in Eq. (2.17). In this section, for simplicity, we omit primes in those equations. Usually, stable solutions of $\vec{J}^{NE}(\vec{M}) = 0$ correspond to the preferred slopes $\vec{M}$ of the facets that develop across the growing interface and organize themselves into large structures [1-4], such as pyramids or rippled interface states discussed here. Our model Eq. (2.17) exhibits all the types of (110) surface current zeros classified in Sec. II: (i) Singlet, $M_1=M_2=0$, as in Fig 2(a); (ii) Doublets of two equivalent (symmetry related) slope vectors as in Fig 2(b). These are the R_1 doublet, at

$$M_1 = \pm\sqrt{1+a}, \quad M_2 = 0, \quad (3.1)$$

and the R_2 doublet, at

$$M_1 = 0, \quad M_2 = \pm\sqrt{1-a}; \quad (3.2)$$

(iii) The Quartet of four equivalent slope vectors, as in Fig 2(c), at

$$\begin{aligned} M_1 &= \pm\sqrt{\frac{1+c+b}{1+c^2-b^2}}\sqrt{a-a_-}, \\ M_2 &= \pm\sqrt{\frac{1-c+b}{1+c^2-b^2}}\sqrt{a_+-a}, \end{aligned} \quad (3.3)$$

with

Fig. 3. Kinetic phase diagram for the multilayer epitaxial growth and erosion on (110) surfaces. For each interfacial state, the figure indicates M -space with stable (full circles) and unstable (empty circles) zeros of the surface nonequilibrium current (see text for details). R_1 and R_2 are the two Rippled states, $R_1^{(rec)}$ and $R_2^{(rec)}$ are the two Rectangular Rippled states, whereas the Buckled Rippled state, $R_1^{(buc)}$, occupies the hatched domain (all its

Fig. 3(cont). current zeros are unstable, as depicted in the inset). For the *RhP* quartet, the angle θ ranges from zero, at the transition to R_1 , to 90° , at the transition to R_2 . Here and in Fig. 4, the phase diagram is given in the (b, a) plane for a fixed value of the parameter c . Here and in the following figures, we set $c = 3/4$ for concreteness. The qualitative details of the phase diagram are independent of the actual value of c , as long as c is nonzero (see the text). Changing signs of both a and c is equivalent to exchanging the spatial coordinates x_1 and x_2 . In effect, for a negative c , the phase diagram would appear as in the figures here reflected across the horizontal axis ($a \rightarrow -a$ reflection). Due to this, for $c = 0$ the phase diagram becomes symmetric under $a \rightarrow -a$, whereas the Buckled Rippled state domain vanishes (see the text). For $a = 0$ and $c = 0$, the exchange of the coordinates x_1 and x_2 becomes the symmetry of the model, i.e., the model acquires the diagonal reflection symmetry, absent on (110) surfaces. This symmetry is however present on (100) surfaces, and, in fact, for $a = 0$ and $c = 0$, the present model reduces to the previously studied model for (100) surfaces in Refs. [1] and [2].

Fig. 4. Kinetic phase diagram for the multilayer epitaxial growth and erosion of (110) surfaces. This figure parallels Fig. 3. Here, for each interfacial state we give basic data from our simulations: surface contour plots, magnitudes of interfacial height Fourier transforms (FT), corresponding to in-phase diffraction patterns, and slope distributions (SD) in the M -space, corresponding to out-of-phase diffraction patterns. R_1 and R_2 are the two Rippled states, RhP is the Rhomboidal Pyramid

Fig. 4(cont). state, $R_1^{(rec)}$ and $R_2^{(rec)}$ are the two Rectangular Rippled states, and $R_1^{(buc)}$ (hatched domain) is the Buckled Rippled state (for it, data are shown in the figures 12 through 16). The RhP rhomboidal angle 2θ ranges from zero, at the transition to R_1 , to 180° , at the transition to R_2 . At long times, the four-lobe FTs of the Rectangular Rippled states approach the two-lobe form of the FTs of ordinary Rippled states (see Sec. IV, and, also, the Fig. 10 caption). Note that the peaks of SD of various states here, obtained from our simulations, directly correspond to the stable zeros of the surface non-equilibrium current in Fig. 3. In this respect, the Buckled Rippled state $R_1^{(buc)}$ (in the hatched area with no stable zeros) is exceptional [for the SD of the $R_1^{(buc)}$ state see Figs. 13 and 16]. As noted in Fig. 3 caption, the phase diagram here is given for a positive value of the parameter c , without lack of generality: Changing signs of both a and c is equivalent to exchanging the spatial coordinates x_1 and x_2 . Thus, in particular, the $R_1^{(buc)}$ state [buckled form of the R_1 rippled state] occurs for $c > 0$, whereas the $R_2^{(buc)}$ state [buckled form of the R_2 rippled state, not shown here] occurs for $c < 0$.

$$a_+ = \frac{1-b+c}{1+b-c}, \quad a_- = -\frac{1-b-c}{1+b+c}. \quad (3.4)$$

The kinetic phase diagram depends only on the three independent parameters a , b , and c in Eq. (2.18). In Figs. 3 and 4, we depict our phase diagram in the (b, a) plane for a fixed c . In the figures, for concreteness, $c = 3/4$. However, the phase diagram does not qualitatively depend on the value of c , as long as $c \neq 0$ (see the following discussions). Fig. 3 gives the stability phase diagram for the zeros of $\vec{J}^{NE}(\vec{M})$ in Eqs. (3.1) to (3.3). Fig. 4, obtained from our simulations of the model Eq. (2.17), gives interface height contour plots, the interface slope vector distributions (SD), and interface height Fourier transforms (FT). The phase diagram in Figs. 3 and 4 is inferred by the stability analysis of facets in Eqs. (3.1) to (3.3) that is outlined in Appendix A. The phase diagram is further corroborated by numerical simulations of the model Eq. (2.17), see Sec. IV. Thus, we find that the R_1 doublet Eq. (3.1) gives rise to the Rippled State R_1 , whereas the R_2 doublet Eq. (3.2) gives rise to the Rippled State R_2 , see Figs. 3 and 4. These rippled interface states are structures of alternating facets of a doublet, e.g., for the R_1 state, the facet $(+\sqrt{1+a}, 0)$ alternates with the facet $(-\sqrt{1+a}, 0)$, see Fig. 5(a). From the stability analysis in the Appendix A, we find that the facets of the R_1 doublet are stable only for a above the line $a_+(b, c)$ in Fig. 3, given by Eq. (3.4) above. Likewise, we find that the facets of the R_2 doublet are stable only below the line $a_-(b, c)$ in Fig. 3, given by Eq. (3.4). The lines $a_+(b, c)$ and $a_-(b, c)$ in Figs. 3 and 4, intersect at the point X located at

$$b_X = \sqrt{1+c^2}, \quad a_X = \left(\sqrt{1+c^2} - 1\right)/c.$$

Fig. 5. 3-d views of various interfacial states from our simulations: (a) Rippled state with the period λ , (b) Rhomboidal Pyramid state with the periods λ_1 and λ_2 , and, (c) Rectangular Rippled state, with the period λ , that has the motif in the form of a roof-like pyramid (hut), with a long roof-top edge of the length ξ .

For, for $b < b_x$, there is the range of the parameter a ,

$$a_-(b, c) < a < a_+(b, c), \quad (3.5)$$

such that both R_1 and R_2 doublets are unstable. In this range of the phase diagram in Figs. 3 and 4, both rippled phases are unstable, see Appendix A. In the Appendix A, we show that there are two types of qualitatively different stability behaviors occurring in the range defined by Eq. (3.5):

(i) For $b < 1$, the quartet Eq. (3.3) is stable for a in the range Eq. (3.5), and, as documented in Sec. IV, it gives rise to a novel pyramidal state we call the Rhomboidal Pyramidal state. This state is a nearly periodic structure made of four-sided pyramids, of the form

$$h(x_1, x_2) = |M_1||x_1| + |M_2||x_2|, \quad (3.6)$$

within a single period, $|x_1| < \lambda_1/2$, $|x_2| < \lambda_2/2$ [see Fig. 5(b) from our simulations]. In Eq. (3.6), (M_1, M_2) are as in Eq. (3.3). By Eq. (3.6), these pyramids have contour lines shaped as rhombs. The rhomboidal angle 2θ , between two selected quartet facets [see Figs. 3 and 4] is given by $\tan \theta = M_2/M_1$. Thus, by Eq (3.3) we find

$$\tan \theta \sim \sqrt{\frac{a_+ - a}{a - a_-}} \quad (3.7)$$

Note, that $\theta \rightarrow 0$, i.e., $M_2 \rightarrow 0$, as $a \rightarrow a_+$. In this limit, in Fig. 3 the *RhP* quartet Eq. (3.3) continuously approaches the R_1 doublet Eq. (3.1). Thus the R_1 -to-*RhP* transition in Fig. (3) and (4) is a Hopf bifurcation. Also, by Eq. (3.7), $\theta \rightarrow 90^\circ$, i.e., $M_2 \rightarrow 0$, as

$a \rightarrow a_-$. In this limit, in Fig. 3, the RhP quartet approaches the R_2 doublet. Thus, the R_2 -to- RhP transition in Figs. 3 and 4 is also a Hopf bifurcation.

(ii) For $1 < b < b_x$ and a in the range Eq. (3.5), i.e., in the region hatched in Fig. 3 and 4, the analysis presented in the Appendix A indicates a stability behavior rather different from the one in the item (i). In the hatched region, it turns out that *all* of the types of zeros of $\vec{J}^{NE}(\vec{M})$, in Eqs. (3.1) to (3.3), are unstable, as indicated in the Fig. 3 insert. This is in contrast to all other interface states entering our phase diagram which have some of the zeros stable. The phase diagram region having all zeros unstable can never occur for the interface dynamics governed by a free energy or by an effective free energy (see Appendix A). We recall that the effective free energy functional exists for our model Eq. (2,17) *only* in the special case $u_{12}=u_{21}$, i.e. $c=0$, see Eqs. (2.12) and (2.13). However, as noted below Eq. (2.11), for (110) crystal surfaces $u_{12} \neq u_{21}$ in *general*. Thus, importantly, the unusual region, hatched in Figs. 3 and 4, with all zeros of $\vec{J}^{NE}(\vec{M})$ being unstable, is actually generic for (110) crystal surfaces. In Sec. IV we show that an unusual interface state develops in this region of the phase diagram in Figs. 3 and 4. This state is characterized by striking presence of persistent surface currents, that are absent in other interfacial states here. We call this uncommon state the Buckled Rippled State (R^{buc}). In contrast to the R^{buc} state, all other states here develop facets vanishing surface non-equilibrium current, i.e., the facets in Eqs. (3.1) through (3.3).

There are two more interfacial states that develop in our model. In Figs. 3 and 4, they are to the right of the X point, $b > b_x$, for the parameter a in the range

$$a_+(b, c) < a < a_-(b, c). \quad (3.8)$$

In this range, the R_1 and R_2 facets in Eqs. (3.1) and (3.2) are *both* stable, while the quartet Eq. (3.3) is unstable. From our simulations in Sec. IV, we find that, in the region Eq. (3.8), interface structures formed out of both R_1 and R_2 facets develop. These structures have rectangular contour lines seen in Fig. 4. As documented by our simulations in Sec. IV, there are two kinds of these structures, called the Rectangular Rippled States $R_1^{(\text{rec})}$ and $R_2^{(\text{rec})}$: In the $R_1^{(\text{rec})}$ state, the R_1 facets grow faster than R_2 facets, whereas in the $R_2^{(\text{rec})}$ state, the R_2 facets grow faster than R_1 facets. The basic motif of both of these states is a roof-like pyramid (hut), with a long roof top edge, see Fig. 5(c) from our simulations. In the $R_1^{(\text{rec})}$ state, this edge develops between long rapidly growing R_1 facets. For the $R_2^{(\text{rec})}$ state, the roof top edge develops between R_2 facets. The difference in the growth rates between R_1 and R_2 facets here is naturally related to the fact that R_1 and R_2 facets are not equivalent to each other. The diagonal reflection which would make them equivalent is not a symmetry of (110) surface, see Eq. (2.10). In particular, this implies that, in general, there is no steady state interface profile ($\partial h/\partial t = 0$) of the dynamics equation (2.1) that would have the form of a static edge between two semi-infinite R_1 and R_2 facets. This is strikingly different from the situation one has for any two quartet facets Eq. (3.3), forming the pyramids of the RhP state, Eq. (3.6). These facets are equivalent to each other, and the static edge (“interface”) between these facets generally exists (see Appendix B). Thanks to this, the four-sided RhP pyramids are structurally stable. On the other hand, the static edge interfacing R_1 and R_2 facets exists only along the special line $a_{cr}(b, c)$ in the phase diagram Fig. 3, given by

$$a_{cr} = \frac{\sqrt{1 + (c/3)^2} - 1}{c/3}, \quad (3.9)$$

see App. B. The critical line Eq. (3.9) actually corresponds to the phase transition between $R_1^{(rec)}$ and $R_2^{(rec)}$ states in Figs. 3 and 4. We detail on this in Sec. IV and Appendix B.

Let us discuss the phase diagram for the special case $c = 0$, i.e., $u_{12} = u_{21}$. Then the dynamics is governed by an effective free energy [see Eqs. (2.12) and (2.13), and Appendix B]. For this case, the phase diagram in the (a, b) plane assumes the form symmetric with respect to $(a, b) \rightarrow (-a, b)$. For $c = 0$, the change $a \rightarrow -a$ is actually equivalent to exchanging x_1 and x_2 , as can be seen from Eq. (2.17) [see, also, Fig. 3 caption]. In particular, R_1 state is then mapped into R_2 state. Likewise, $R_1^{(rec)}$ is mapped into $R_2^{(rec)}$ and the transition line between them becomes simply $a_{cr} = 0$, in accord with Eq. (3.9) for $c \rightarrow 0$. In this limit, the X point in Figs. 3 and 4 is located on the symmetry line $a = 0$, at $b_X = 1$. For $c \rightarrow 0$, the Buckled Rippled state occurring in the hatched area in the range $1 < b < b_X$ [see Fig. 3] disappears, as then $b_X = \sqrt{1 + c^2} \rightarrow 1$. This state disappears for $c = 0$, because the interface dynamics is then governed by the effective free energy with the non-equilibrium surface current generated by the potential Eq. (2.12b). The existence of $U(\vec{M})$ for this case, excludes the situations with all zeros of $\vec{J}^{NE}(\vec{M})$ being unstable, see Appendix A. Thus, the unusual $R^{(buc)}$ state region, which has all zeros unstable, disappears for $u_{12} = u_{21}$, i.e., for $c = 0$.

An important aspect of the epitaxial growth is the selection of the slope vectors of the faceted states developing across the interface. In many of the previous studies, the selected slope vectors are simply assumed to correspond to the zeros of non-equilibrium

current $\vec{J}^{NE}(\vec{M})$. This assumption is necessarily true only if the interface dynamics governed by an effective free energy: By Eqs. (2.12) and (2.13) one can easily show that

$$\frac{dF_{eff}}{dt} = - \int d^2x \left(\frac{\partial h(x,t)}{\partial t} \right)^2 \leq 0. \quad (3.10)$$

Thus, the effective free energy F_{eff} generally decreases in time. This free energy minimization process is achieved by breaking up the interface into growing facets: on the flat facet the surface diffusion “free energy” F_{sd} in Eq. (2.13c) reduces to zero, whereas the non-equilibrium current free energy Eq. (2.13b) is minimized by selecting the slopes that minimize the local potential $U(\vec{M})$. By Eq. (2.12a), this further means that the non-equilibrium current $\vec{J}^{NE}$ vanishes at the selected slope vectors. On the other hand, in our model here, unless $c = 0$, there is no free energy governing the interface dynamics. Thus, it is not assured that interface structures have facets vanishing the non-equilibrium current. This is evidenced here by the existence of our $R^{(buc)}$ state which indeed exhibits persistent surface currents (see Sec. IV). Nonetheless, with this important exception, for all other states of our model we find that the selected facet slopes $\vec{M}$ are zeros of $\vec{J}^{NE}(\vec{M})$.

IV. INTERFACIAL STATES

In this section we discuss the properties of the multitude of interfacial states introduced in Sec. III. As it was anticipated there, the stable *quartet* $(\pm M_1, \pm M_2)$ gives rise to *two-dimensionally* periodic interface structures of four-sided pyramid-like objects in Fig. 5(b). The form of these objects is given by Eq. (3.6). By the Eq. (3.6), the contour lines (i.e., step terraces) of these pyramids are *rhombi* (or rhomboids, if roof-top edges develop on the pyramids, see Fig. 6). Thus, it is called the Rhomboidal Pyramid (*RhP*) state. This state, predicted by us in Ref. [3], has been subsequently seen by de Mongeot *et al.*, in the epitaxial erosion on both Cu(110) and Rh(110) surfaces, [13]. Typical for the *RhP* state is the slope distribution (SD), i.e., out-of-phase diffraction pattern, with the quartet of four equivalent peaks $(\pm M_1, \pm M_2)$, see Fig. 4 and 7. By the *RhP* motif in Eq. (3.6), squared magnitude of the Fourier transform (FT) of the *RhP* 2-d periodic surface, $|\tilde{h}(q_1, q_2)|^2$ is easily shown to have dominant peaks placed along the q_1 and q_2 axes: (i) the set of peaks at the wave-vectors $(\pm 2\pi(2n+1)/\lambda_1, 0)$, with the integrated intensities $I_n^{(1)} \sim (M_1\lambda_1)^2(2n+1)^{-4}$, $n = 0, 1, 2, \dots$; (ii) the set of peaks at $(0, \pm 2\pi(2n+1)/\lambda_2)$ with the integrated intensities $I_n^{(2)} \sim (M_2\lambda_2)^2(2n+1)^{-4}$, $n = 0, 1, 2, \dots$. Structurally, by the Eq. (3.6) the *RhP* state has the form of a linear superposition of the two rippled states. Thus, its FT, i.e., in-phase diffraction pattern is essentially the superposition of the FTs of the two rippled states R_1 and R_2 [see Fig. 4]. Notably from our simulations, (at most) the four brightest ($n=0$) among the peaks, at the wave-vectors $(\pm 2\pi/\lambda_1, 0)$ and $(0, \pm 2\pi/\lambda_2)$ are visible [see Fig. 6]. Such a four-lobe in-phase diffraction pattern is

Fig. 6. Rhomboidal Pyramid (*RhP*) state: To the left are the interface contour plots. To the right are the facet edges plots (contour plots of the magnitude of local interface curvature), with prominently present dislocations destroying perfect periodicity of the interface profile. In Fig. (a), we give the ordinary *RhP* state, occurring away from the *RhP*-to- $R_1^{(buc)}$ transition. In Fig. (b), we give the intensely rough *RhP* state, occurring close to this transition [see also Fig. 7; the interface here corresponds to the maximally rough surface found at $a = 0.6$]. The interface structure is notably positionally disordered and, also, highly anisotropic, as reflected in Fig. (b) by the presence of sharp vertical edges and roof-top edges (dark), and blunt horizontal edges (faint). Note the qualitative difference between the Fourier transforms (FT) in Figs. (a) and (b). In the intensely rough *RhP* in Fig. (b), only one pair of FT peaks is seen – the other pair [seen in (a)] is suppressed due to large positional disorder of the vertical edges.

Fig. 7. (a) The square of the interfacial width $\langle h^2 \rangle$ versus the parameter a , given for several different times, across the transition from the Rippled state R_2 (for $a < a_-$) to the Rippled State R_1 (for $a > a_+$), going through the intermediary Rhomboidal Pyramid state (occurring for $a_- < a < a_+$). The Fig. (a) is obtained from numerous simulations done along the line $b = 0.8$ that passes close to the transition line $b = 1$ from the RhP to the $R_1^{(buc)}$ state (see Figs. 3 and 4). The inset documents the enhanced roughening of the RhP state, with the roughening exponent reaching the value ≈ 0.4 close to the center of the RhP range, at $a = 0.6$. In Fig. (b), we give Fourier transform magnitudes (FT) and Slope Distributions (SD) found along this ripple rotation transition, for $a = 0$ [in the R_2 state], and for $a = 0.4$ and 0.8 [both within the intensely rough RhP range]. Note that FT's, i.e., in-phase diffraction patterns of the intensely rough RhP are with just one pair of peaks, like the R_1 pattern. The other, significantly weaker pair of peaks can be seen only close to the transition to R_2 [see $a = 0.4$ here]. Note that SD's, i.e., the out-of-phase diffraction patterns [to the right in Fig. (b)] distinguish the RhP from the R_1 state [see also Fig. 4].

manifested in the *RhP* FT magnitude plots in Figs. 4 and 6(a), from our simulations. All other peaks are smeared by the positional disorder of the pyramid lattice. This disorder is especially pronounced in the *RhP* region close to the $R_1^{(buc)}$ state. Therein, the *RhP* in-phase diffraction pattern exhibits only two peaks [unless very close to the *RhP*-to- R_2 transition, see Figs. 6(b) and 7(b), and the discussions in the following]. Such a nearly two-lobe *RhP* in-phase diffraction pattern has been indeed seen in the recent study that has revealed our *RhP* state in erosion on Cu(110) and Rh(110) crystal surfaces [13].

The *RhP* state is characterized by (nearly) rectangular network of pyramid facet edges, see Fig. 6. The coarsening dynamics of the *RhP* state is similar to that of the square pyramid Phase I (with the square network of edges) on (001) surfaces, [1, 4]. The coarsening is mediated by motion and annihilations of the dislocations of the network of pyramid facet edges seen in Fig. 6. In accord with this, we find that the interface width, $w = \langle h^2 \rangle^{1/2}$, grows as $w \sim t^\beta$, with $\beta \approx 1/4$, [1,4]. Such a coarsening was found *away* from the transitions to other interface states in Figs. 3 and 4 [see Fig. 6(a)]. However, a substantially faster coarsening was found in the *RhP* region close to the $R^{(buc)}$ state (the hatched domain in Figs. 3 and 4, discussed later on). This enhanced roughening of *RhP* is documented in Fig. 7(a), which gives the interface width w , for several different times, versus the parameter a (for a fixed $b < 1$). In this figure, the *RhP* state occurs between the vertical lines at a_+ and a_- , whereas for $a < a_-$ the rippled phase R_2 , and for $a > a_+$ the rippled phase R_1 occurs. The fastest coarsening was found within the *RhP* state range, $a_- < a < a_+$, see Fig 7(a). Therein, at the longest times, the *RhP* pyramids grow with a high coarsening exponent $\beta \approx 0.4$, see Fig 7(a). Such an enhanced roughening of the *RhP* intermediary state (faster than that of the nearby rippled states, see below) has been

observed also in the aforementioned experiments on Cu(110) and Rh(110) surfaces, [13]. We stress that the enhanced roughening of *RhP* occurs only in the proximity to the $R^{(buc)}$ state in Fig 3 and 4. There the *RhP* state becomes highly anisotropic. This is documented in Fig. 6(b) where we see that the two *RhP* state periods λ_1 and λ_2 [along the principal axis of (100) surface, see Fig. 5] significantly differ from each other. This anisotropy is manifested also from the character of the pyramid edges seen in Fig. 6(b). Vertical edges are sharp and connected to each other (either directly or by frequently present roof-top edges seen in Fig. 6(b)). In contrast to this, the horizontal edges in Fig. 6(b) are blunt and disconnected from each other. Due to this positional disorder of horizontal edges, the intensely rough *RhP* structure in Fig. 6(b) is significantly more disordered than the usual *RhP* structures seen in Fig. 6(a). Its enhanced roughening is similar to the fast roughening seen in the nearby $R^{(buc)}$ state, discussed later in this section. Both the intensely rough *RhP* and the $R^{(buc)}$ state exhibit two-lobe in-phase diffraction patterns (i.e., FT's), see Figs. 6(b) and 7(b), as well as the figure 16 later on. Having the two-lobe [rather than the four-lobe] FT pattern is a consequence of the typically large aspect ratio λ_1 / λ_2 , and also, of the strong positional disorder of vertical facet edges manifest in Fig. 6(b). Indeed, by our previous discussions of the peak intensities, $I_0^{(2)} / I_0^{(1)} = (M_2 \lambda_2)^2 / (M_1 \lambda_1)^2$, so for $\lambda_2 \ll \lambda_1$ the peak pair at $(q_1 = 0, q_2 = \pm 2\pi / \lambda_2)$ is much weaker than the peak pair at $(q_1 = \pm 2\pi / \lambda_1, q_2 = 0)$. The weaker peak pair is thus easily depressed by the positional disorder seen in Fig. 6(b). In effect, the intensely rough *RhP* state exhibits the two-lobe in-phase diffraction patterns seen in Fig. 6(b) and 7(b).

Thus, importantly, the intensely rough *RhP* state has nearly the same in-phase diffraction pattern as a simple rippled state. This feature, seen in the experiments on Cu(110) and Rh(110) surfaces [13], is documented here in Fig. 7(b) from our simulations. Note that this FT, i.e., the in-phase diffraction pattern is nearly the same as that of the R_1 rippled state [unless close to the transition to the R_2 rippled state, see Fig. 7(b), middle panel]. Due to this feature, the out-of-phase diffraction pattern, i.e., slope distribution from our simulations [see Fig. 7(b), right panel], with the quartet of four equivalent peaks is essential for the identification of our *RhP* state in recent experiments on Cu(110) and Rh(110) surfaces [13]. Our R_1 state here corresponds to the “hot rippled state” (the high temperature one), whereas the experiments indeed show that the *RhP* has the same FT as the “cold ripple state” seen in [13].

We now proceed to discuss the properties of the Rippled states R_1 and R_2 . From our simulations we find that the coarsening of the rippled states is mediated by moving dislocations that destroy the perfect periodicity of these structures. See Fig. 8 giving the interface in terms of the edges formed between alternating R facets [see, also Fig. 5(a)]. The dislocations of Rippled states R_1 and R_2 are somewhat similar to the dislocations of 2-d smectic A liquid crystals, [15]. Here, however, the dislocations are prominently dynamical objects. They move (climb) along the direction of facet edges in Fig. 8. This motion is driven by the edges tensions which are unbalanced at the dislocations cores. In Figs. 8(a) and (b) we see two morphologically different types of dislocations: (i) “forks”, with three edges on one side of the core and just one edge on the opposite side; (ii) “knives”, with two edges on one side and no edges on the opposite side of the core. Thus, in both cases, there are extra two edges pulling dislocations. This misbalance of edges

Fig. 8. (a) Facet edges plot of the Rippled state R_1 in the parameter range where both fork- and knife-dislocations are present. (b) Facet edges plot of the Rippled state R_2 in the parameter range where only knife-dislocations are present. Note that the R_2 state in Fig. (b) is rotated by 90° to facilitate comparison with Fig. (a). The length scale ξ is the average distance between dislocations along a ripple. See the text for discussions.

tensions causes the dislocations to move along the ripples (vertically in Fig. 8). Importantly, we find that this dislocation motion (climb) mediates the growth of the ripple phase period λ : As the dislocation moves along the extra edges, it leaves behind enlarged facets [compare the facet width just above and below dislocations in Figs. 8(a) and (b)]. Thus, the growth of the rippled phase period λ is nothing else but the fusion of the rippled state R facets mediated by climbing dislocations in Figs. 8(a) and (b). In addition to the interface width w and the average ripple period λ , we find that the rippled states are characterized also by the *coherence length* of ripples, ξ , corresponding to the separation between dislocations along a ripple (see Fig. 8). The ripple coherence length ξ increases with time because of annihilations of pairs of dislocations traveling towards each other in Fig. 8. Due to the annihilations, the number of dislocations decreases, and the ripple coherence length ξ increases in time. Both λ and ξ are extracted from our simulations by using the anisotropic correlation function

$$K(x_1, x_2, t) = \langle h(x_1, x_2, t) h(0, 0, t) \rangle = (w(t))^2 \psi(x_1 / \lambda(t), x_2 / \xi(t)), \quad (4.1)$$

for the R_1 phase. In Eq. (4.1), the function ψ decays in an oscillatory fashion along x_1 [longitudinal correlations], and monotonously along x_2 [transversal correlations], see Fig. 9(a) for details. By using the longitudinal and transversal correlations, from our simulations we find that $\lambda \sim w$ and ξ grow as power laws of time,

$$w \sim \lambda \sim t^{n_\lambda}, \quad \xi \sim t^{n_\xi}. \quad (4.2)$$

Regarding the values of the coarsening exponents n_λ and n_ξ , we have revealed *two* kinetically different subdomains of the whole rippled phase domain in the phase diagram in Fig. 4. The two subdomains are characterized by different morphologies and kinetics

Fig. 9. (a) Rippled states interface height-height correlation functions $K(x_1, x_2, t)$, for the case of the R_1 state: Longitudinal correlations $K_{long}(x_1, t) = K(x_1, x_2 = 0, t)$, used to find the average phase period $\lambda(t)$, and transversal correlations $K_{trans}(x_2, t) = K(x_1 = 0, x_2, t)$ used to find the ripple coherence length $\xi(t)$. [For the R_2 state, x_1 and x_2 are to be switched in the above statements.] (b) $\lambda(t)$ and $\xi(t)$ for the rippled phase with both knives and forks present [as in Fig. 8(a)]. (c) $\lambda(t)$ and $\xi(t)$ for the rippled phase with only knives present [as in Fig. 8(b)]. In Fig. (d) we depict topological changes (knife-to-fork-to-knife transitions), causing the dislocation to randomly glide by one half of the ripple phase period (pay attention on the numbers counting facet edges in the figure). Such a dislocation glide is prohibited if fork formation is suppressed, as in the rippled state in Fig. 8(b).

of moving dislocations, as illustrated in Figs. 8(a) and (b). Most of our phase diagram in Fig. 4 is occupied by the rippled phase with the dislocations depicted in Fig. 8(a). In this figure, we see both forks and knives climbing along the x_2 direction. In addition to this directed climbing motion, our simulations reveal that dislocations move also along the x_1 direction in Fig. 8(a). In contrast to the dislocation climb, this dislocation glide motion along x_1 is random and it involves reconnection (topology changes) of the edges network, turning forks into knives and vice versa. See Fig. 9(d) depicting this dislocation glide type motion seen in our simulations. There we see a knife turning into a fork, which then turns into a knife, the position of which is displaced by one half of the rippled phase period (with respect to the position of the original knife). In the subdomain of the phase diagram in which such a mechanism of dislocation glide is active, we find that the λ and ξ grow as in Eq. (4.2) with $n_\lambda = 2/7$ and $n_\xi = 4/7$, as documented in Fig. 9(b) from our simulations, and further corroborated by analytic arguments elsewhere [16]. Our simulations however reveal the existence of another subdomain of the kinetic phase diagram in Fig. 4, in which the coarsening of the rippled phase goes with different exponents, $n_\lambda = 1/3$ and $n_\xi = 1/2$, see Fig. 9(c). This scaling was found to occur for $c \neq 0$ in a range below the *RhP* domain in Fig. 4 [e.g., for a below a_- , i.e., below the intensely rough *RhP* in Fig. 7(a)]. Therein, the reconnections of facet edges (i.e., the formations of forks) are suppressed, as documented in Fig. 8(b) from our simulations in which only the knife-dislocations are seen. Consequently, the dislocation glide motion [Fig. 9(d)] is prohibited in this subdomain of the phase diagram. This dynamical constraint yields the aforementioned exponents $n_\lambda = 1/3$ and $n_\xi = 1/2$, as documented in Fig. 9(c), and further corroborated by analytic arguments elsewhere [16].

In addition to passing through the RhP and the $R^{(buc)}$ states, the transition between the rippled states R_1 to R_2 may go also through the Rectangular Rippled states, $R_1^{(rec)}$ and $R_2^{(rec)}$ in Figs. 3 and 4, see also Fig. 5(c). Within the range of these $R^{(rec)}$ states, the two *non-equivalent* doublets $(\pm M_1, 0)$ and $(0, \pm M_2)$, Eqs. (3.1) and (3.2), giving rise to the facets of R_1 and R_2 , are *both* locally stable (i.e., one has a multistable region, see Sec. III discussions). These facets comprise the basic motif of the two $R^{(rec)}$ states, that is a roof-like pyramid (hut) with a *rectangular* base $\lambda \times \xi$, yielding rectangular contour lines, see Figs. 4, 5(c), 10, 11 from our simulations. We stress that our basic Rectangular Rippled state structure, the checkerboard arrangement of huts and pits (inverted huts) has been clearly seen in the erosion experiments on Ag(110), by Constantini *et al.* [see Fig. 4(d) in Ref. 10, and compare with our Figs. 4 and 11]. The hut base sizes λ and ξ are along the two (non-equivalent) principal directions of (110) surface. We find them grow in time with *different* power laws: $\lambda \sim t^{n_\lambda}$, with $n_\lambda = 1/4$, and $\xi \sim t^{n_\xi}$, with $n_\xi = 1/2$, as obtained from the longitudinal and transversal correlations [Fig. 10(a)]. As $w(t) \sim \lambda(t) \ll \xi(t)$ at long times, such rectangular pyramid states are a special kind of rippled states with the period $\lambda(t)$. This is evidenced also by their Fourier transforms, i.e., in-phase diffraction patterns seen in Fig. 4. They have four peaks, at $(\pm q_1, \pm q_2)$, with $q_1 \sim 1/\lambda$ and $q_2 \sim 1/\xi$, for the $R_1^{(rec)}$ state. However, as $\xi(t) \gg \lambda(t)$, this diffraction pattern approaches in time the form of the in-phase diffraction pattern of the nearby rippled R_1 state with just two peaks at $(\pm q_1, 0)$. The length scale $\xi(t)$ is essentially the length of the long roof-top edges present on these roof-like pyramids, see Figs. 11 and 5(c). These roof-top edges develop and grow either along the x_2 direction in

Fig. 10. Rectangular Rippled State: (a) Longitudinal and transversal correlations (at two different times) used to obtain the structural length scales $\lambda(t)$ and $\xi(t)$ [see also Figs. 5(c), 9(a), and 11]; (b) Corresponding snapshots of facet edges plots of the $R_2^{(rec)}$ state and interface FTs at two different times. Note the presence of rapidly growing horizontal roof-top edges interfacing the dominant R_2 facets [see, also, Fig. 5(c)]. These roof-like pyramids (huts) are terminated on both sides by small

Fig. 10(cont). rhomboidally shaped R_1 facets. Prominent feature of the Rectangular Rippled state is that these diamond like R_1 facets cluster to form long chains. Due to the presence of these chains, the interface structure of the $R^{(rec)}$ states is more coherent than that of ordinary rippled states. At early times, Rectangular Rippled states appear quasi-periodic not only along the $\hat{\lambda}$ direction but also along the $\hat{\xi}$ direction (unlike the ordinary rippled phase): Note that, at early times, the transversal correlations in Fig. (a) here oscillate [unlike to those of the ordinary rippled state in Fig. 9(a)]. However, with increasing time, the number of R_1 facets incorporated in individual chains decreases and, also, the chains are less evenly spaced, as seen in the figures here. Due to this, the coherence of the Rectangular Rippled structure along the transversal direction (parallel to ripples) decreases in time and becomes comparable to that of ordinary rippled state. This is manifested in the loss of oscillations in the transversal correlations [see Fig. (a) here at the long time and compare with Fig. 9(a)]. Related to this, at long times, the four FT peaks of the Rectangular Rippled state in Fig. (b) (left panel), merge into just two peaks in Fig. (b) (right panel) and such FT becomes indistinguishable from that of the ordinary Rippled state in Fig. 4.

Fig. 11. Sequence of interfacial states occurring in the $R_1^{(rec)}$ [Fig. (a)] to $R_2^{(rec)}$ [Fig. (c)] transition (interface contour lines and corresponding facet edges plots). For $a > a_{cr}$, one has the $R_1^{(rec)}$ state with roof top edges growing vertically in the Fig. (a). For $a < a_{cr}$, one has the $R_2^{(rec)}$ state with roof top edges growing horizontally in the Fig. (c). At the critical point $a = a_{cr}$, four-sided rectangular pyramids develop with no roof-top edges present, as shown in Fig. (b). See text for details.

the $R_1^{(rec)}$, or along the x_I direction in the $R_2^{(rec)}$ state, see Fig. 11(a) and (c). The roof-top edges do not develop only along the transition line between $R_1^{(rec)}$ and $R_2^{(rec)}$ states in Figs. 3 and 4. Along this transition line, simple four-sided pyramids [without roof-top edges] develop, with a rhomboidal network of edges, see Fig. 11(b). This critical state is an anisotropic version of the square pyramid Phase II on (100) surfaces [1,4]. Its in-phase diffraction pattern also has four peaks $(\pm q_1, \pm q_2)$, with $q_1 \sim q_2 \sim 1/t^{1/4}$. The $R_1^{(rec)}$ -to- $R_2^{(rec)}$ transition line is a far-from-equilibrium first order like transition at which the two non-equivalent doublets of (110) surfaces [see Eqs. (3.1) and (3.2), and Fig. 2(b)], giving rise to R_1 and R_2 states, coexist. As discussed in Sec. III and App. B, this Gibbs like coexistence requires the existence of the stationary solution $(\partial h/\partial t = 0)$ of Eq. (2.1) being the static interface (edge) between *infinite* R_1 and R_2 facets. This requirement yields our analytic prediction for the position of the $R_1^{(rec)}$ -to- $R_2^{(rec)}$ transition line given in Eq. (3.9), which is corroborated by the simulations in Fig. 11. Main features of the ripple rotation transition seen on Ag(110) surface (growth) [9] correspond to those of our $R_1^{(rec)}$ -to- $R_2^{(rec)}$ transition. Importantly, our study shows that in the multistable region (suggested by the experiments Ref. [9]) one deals *not* with simple rippled phases (R_1 and R_2) but rather with more complex structures, the Rectangular Ripple states. We note that the intermediary state seen on Ag(110) has in-phase diffraction pattern different from that of the critical state seen in Fig. 11(b). Still, the experimental out-of-phase pattern is the same as for the state in Fig. 11(b). As we will discuss elsewhere [17], the experimental in-phase diffraction pattern emerges due to an interesting effect of the vertical growth asymmetry (see also Refs. [4], [5] and our discussion at the end of App. B here).

Our model exhibits one more state, the aforementioned Buckled Rippled $R^{(buc)}$ state that occupies the hatched region in Figs. 3 and 4. Therein, as discussed in Sec. III and the Appendix A, *all* zeros of $\vec{J}^{(NE)}(\vec{M})$ are *unstable* (in contrast to the rest of the phase diagram, with at least some zeros stable). The very existence of such a state escapes the common wisdom that the stable facets with vanishing $\vec{J}^{(NE)}(\vec{M})$ dominate the epitaxial growth and erosion with slope selection (as no facet is stable here!). In the region of our $R^{(buc)}$ state in Figs. 3 and 4, we find a long transient involving ordering of pyramidal chains, see Fig. 12. The interface eventually selects the shape of a rippled phase with buckled (wavy) ripples, structurally similar to the RhP state, see Figs. 13 and 14. $R^{(buc)}$ has a motif similar to that of RhP , Eq. (3.6), however with M_1 and M_2 therein *not* corresponding to a zero of $\vec{J}^{(NE)}(\vec{M})$, see Fig. 13. Thus, strikingly, in contrast to the RhP and all other states discussed here, the facets of the $R^{(buc)}$ state do not assume slopes that vanish $\vec{J}^{(NE)}(\vec{M})$, see Figs. 13 and 14. As documented in Fig. 14, these facets carry non-vanishing, *persistent* downhill surface currents flowing horizontally in Fig. 13(b) [left panel]. The downhill currents in the $R^{(buc)}$ facets are compensated by uphill currents in the horizontal faint edges in Fig. 13(b), see Figs. 13, 14(a) and (b). The distribution of interface slope vectors $P(M_1, M_2, t)$ approaches a stable form peaked *off* the zeros of $\vec{J}^{(NE)}(\vec{M})$, see Fig. 13(b). Thus, the uncommon $R^{(buc)}$ state *does* exhibit the slope selection although there are no stable zeros of $\vec{J}^{(NE)}(\vec{M})$. We find the $R^{(buc)}$ state to exhibit a fast coarsening seen in Fig. 12(a): the interface width $w \sim t^\beta$, with $\beta \approx 0.4$ close to the center of the $R^{(buc)}$ range in Fig. 4. As discussed earlier in this section, a similar enhanced roughening is found in the RhP phase, in the proximity to the $R^{(buc)}$

Fig. 12. Buckled Rippled state. (a) Its interfacial width $w = \langle h^2 \rangle^{1/2}$ grows rapidly in time, $w \sim t^\beta$ with a high coarsening exponent $\beta \approx 0.4$. (b) Time evolution of the interface, through its contour plots (left) and facet edges plots (right). Note that a regular structure develops at long time scales [see the text and Figs. 13 through 14].

a)

b)

Fig. 13. Comparison between the Rhomboidal Pyramid state [Fig. (a)] and the Buckled Rippled state [Fig. (b)]. They have very similar interfacial morphology; see the left panels with the interfacial contour plots and corresponding facet edges plots. Their slope distributions in M -space (right panels) are thus qualitatively the same. However, these two slope distributions document also a striking difference between these two states: For both states, we put the quartet zeros of the surface non-equilibrium current along the dashed lines guiding eye. Note, from Fig. (b) panel, that the Buckled Rippled state selects facets with slopes that are *off* the zeros of the current indicated here by open circles. This is unlike the normally behaved Rhomboidal Pyramid state in Fig. (a). Facets of the Buckled Rippled state thus carry persistent surface currents (see the text and Fig. 14).

Fig. 14. Persistent surface currents [Fig. (b)] in the Buckled Rippled state, $R_1^{(buc)}$ [Fig. (a)]. In Fig. (b) we plot the current J_1 versus x_2 in the $R_1^{(buc)}$ state. Note, from Figs. (a) and (b), that the persistent current is down-hill along the $R^{(buc)}$ facets and it is up-hill along the edges between the facets. This reflects a vortex-like behavior of the surface current - the current goes up the edges and circles back down along the facets. For comparison, in Fig. (b) we also plot (by the dashed line) the surface current J_1 for the ordinary rippled phase [Fig. (c)] as obtained from our simulations. This current is essentially zero at long times when the facets become large. Unlike to this, the facets of the Buckled Rippled state carry non-zero surface currents.

a)

b)

Fig. 15. (a) The interface contour plot obtained at the X point [see Figs. 3 and 4]. Note that the interface has the long-range arrangement of huts and pits of the $R_1^{(rec)}$ state, which is just to the right of the X point. (b) The interface contour plot obtained in the $R_1^{(buc)}$ state. Note that the interface has the spatial arrangement of huts and pits which is the same as at the X point. [X point terminates the $R_1^{(buc)}$ range on its right hand side, see Figs. 3 and 4.] Thus, the $R_1^{(buc)}$ state is essentially the buckled form of the Rectangular Rippled state $R_1^{(rec)}$.

domain in our kinetic phase diagram in Fig. 4 (see Fig. 7 and the discussions). Our simulations have revealed another interesting structural aspect of the Buckled Rippled state, documented in Fig. 15: This state is actually the buckled form of the Rectangular Rippled state. In Fig. 15(b), one can see that the large scale morphology of the $R^{(buc)}$ state is that of the $R^{(rec)}$ state, with large huts and pits (inverted huts) forming a checkerboard structure. In contrast to the $R^{(rec)}$ state, the huts and pits of the $R^{(buc)}$ state are buckled, i.e., exhibit an additional modulation with a wavelength much smaller than the size of huts. The short-scale buckling deformation of the $R^{(buc)}$ state disappears as the X point in phase diagram in Fig. 4 is approached [see Fig. 15(a) and the discussions in the figure caption]. At the X-point, the interface morphology is that of the $R^{(rec)}$ state, see Fig. 15(a).

Structurally and, also, according to its position in the phase diagram in Figs. 3 and 4, the $R^{(buc)}$ state may also qualify to be the intermediary state seen in the erosion on Cu(110) and on Rh(110) surfaces [13]. This is documented by our simulations in Fig. 16, which depict details of the ripple rotation transition along a line going through the $R_1^{(buc)}$ state. The figure is, overall, similar to Fig. 7, in which this transition goes through the intensely rough RhP state. Thus, by comparison with the in-phase and out-of-phase diffraction data on Cu(110) and Rh(110) surfaces [13], we argue that these ripple rotation transitions go with the intervention of either intensely rough RhP [as in Fig. 7] or the $R_1^{(buc)}$ state [as in Fig. 16]. In addition to the diffraction data, this statement is supported also by the fact that both the RhP and $R_1^{(buc)}$ exhibit the experimentally seen enhanced coarsening with the interface width $\sim t^{0.4}$. In both cases, the experimentally seen hot-rippled phase corresponds to our R_2 phase. By decreasing the temperature T , the R_2 facets destabilize, and the interface transforms into the RhP or into the $R_1^{(buc)}$ state. At this

Fig. 16. (a) The square of the interfacial width $\langle h^2 \rangle$ versus the parameter a , given for several different times, across the transition from the Rippled state R_2 (for $a < a_-$) to the Buckled Rippled State $R_1^{(buc)}$ (for $a > a_-$). This transition does not involve an intermediary state. The Fig. (a) graph is obtained from numerous simulations done along the line $b = 1.1$ that goes from R_2 directly to $R_1^{(buc)}$ state. In Fig. (b), we give Fourier transform magnitudes (FT) and Slope Distributions (SD) found along this ripple rotation transition, for $a = 0.2$ [in the R_2 state], and for $a = 0.38$ and 0.44 [both within the $R_1^{(buc)}$ range]. Note that FT's, i.e., in-phase diffraction patterns of the $R_1^{(buc)}$ have just two peaks [like the R_1 pattern]. Still, SD's, i.e., the out-of-phase diffraction patterns [to the right in Fig. (b)] distinguish the $R_1^{(buc)}$ from the R_1 state. Overall, FTs and SDs of the $R_1^{(buc)}$ state here are similar to those of the intensely rough RhP state in Fig 7(b). However, note that the forms of SDs of $R_1^{(buc)}$ are closer or even indistinguishable from that of the R_1 state [see SD obtained at $a = 0.44$ here, still within the $R_1^{(buc)}$ range].

point, it is illuminating to recall of our Fig. 3, and the fact that the R_2 -to- RhP transition is a Hopf bifurcation in which R_2 facets destabilize and newborn RhP facets take over the interface morphology [see Sec. III and App. A]. Microscopically, this facet destabilization with decreasing T can be caused by the Schwoebel barriers on the kinks on the terrace steps of the R_2 facets. These kinks are easily rounded by adatoms only at high enough T (so R_2 is stable there). With decreasing T , the R_2 facets destabilize due to the Schwoebel barriers, and the R_2 rippled state transforms into the RhP state. Likewise, a further decrease of temperature can destabilize the RhP facets and cause the transition into the fascinating $R_1^{(buc)}$ state that has *all* facets unstable [see again our Fig. 3].

Based on this discussion of the microscopic effects underlying our phenomenological model, we argue that the interface morphology transformations seen on Cu(110) and Rh(110) surfaces [13] reflect one (or both) of the following two chains of far-from-equilibrium transitions:

Chain 1: with decreasing T ,

$$R_2 \rightarrow RhP \rightarrow R_1^{(buc)}; \quad (4.3)$$

Chain 2: with decreasing T ,

$$R_2 \rightarrow R_1^{(buc)}. \quad (4.4)$$

In both chains, the R_2 rippled state is the “hot rippled” state, and the $R_1^{(buc)}$ is the “cold rippled” state. Chain 1 has the intensely rough RhP as the intermediary state, manifested through the experimentally seen quartet slope distribution [see our Fig. 7(b)]. On the other hand, the Chain 2 in Eq. (4.4) has *no* any intermediary state involved. Nonetheless, this chain also reproduces the experimental fact that the quartet slope distribution is seen

in an intermediary temperature range. This is documented by our simulations in Fig. 16 here, which gives the in-phase (FT) and out-of-phase (SD) diffraction patterns for the Chain 2, with only R_2 and $R_1^{(buc)}$ states involved. Note that the SD of the $R_1^{(buc)}$ changes from the quartet form [occurring close to the R_2 -to- $R_1^{(buc)}$ transition] to the R_1 -like doublet form, occurring *even before* the to $R_1^{(buc)}$ -to- R_1 transition is reached. Thus, strikingly, the fascinating Rippled Buckled state $R_1^{(buc)}$ reproduces the behaviors observed both in the intermediary (RhP -like) and in the ultimate low temperature (R_1 -like) regime seen in the experiments [13].

V. EFFECTS OF VERTICAL GROWTH ASYMMETRY

In this section, we theoretically elucidate effects of the so-called *vertical asymmetry* (VA) on the growth and erosion on (110) crystal surfaces. The VA is ubiquitously present in realistic systems: the up-down reflection, $h \rightarrow -h$, is not a symmetry of the realistic interface dynamics. In particular, for example, in the growth on (100) crystal surfaces, the VA breaks the up-down symmetry, $h \rightarrow -h$, between pyramids and pyramidally shaped pits, see Ref. [4] and Ch. 4 of this thesis. As discussed there, under some circumstances, the VA effects can be ignored [for example the inclusion of VA does not affect coarsening exponents]. However, in some situations, the VA may qualitatively affect the interface morphology and the behavior of the growth and erosion on crystal surfaces.

Here, we reveal that the VA is essential for understanding the experiments that have reported the ripple rotation transition on the Ag(110) crystal surface [9]. As noted in Sec. IV, within our theory this transition is elucidated as the transition between two Rectangular Rippled States, $R_1^{(rec)}$ and $R_2^{(rec)}$. Within our model, like in the experiments on the Ag(110) epitaxial growth [9], the transition occurs within a multi-stable system parameter range in which R_1 and R_2 facets are both stable. The slopes of these facets, as obtained from our model [see Eqs. (3.1) and (3.2)] are depicted in Fig. 17(a) versus the temperature-like parameter a . The slope behaviors seen in our Fig. 17(a) are in a remarkable qualitative agreement with the non-trivial slope behaviors found in Ref. [9] (see Fig 3(a) therein), provided one makes a (natural) assumption that our parameter a is a monotonous function of substrate temperature. As detailed here, other experimental

Fig. 17. Effects of the VA across the transition from the $R_2^{(rec)}$ to $R_1^{(rec)}$ state. Upper panel: Variations of the slopes of the R_1 and R_2 facets, respectively, $M_1 = \sqrt{1+a}$ and $M_2 = \sqrt{1-a}$, versus the temperature-like dimensionless parameter a . Facet slope is given by a thick line if the facet is stable, and by thin line if the facet is unstable. Both R_1 and R_2 facets are stable for a in the range $a_+ < a < a_-$. Lower panel: Variation of the square of the interface width, $\langle h^2 \rangle$, given for several different times, versus the parameter a . Labeled are the four characteristic values of a , namely, $a_3 < a_2 < a_1 < a_0$, discussed in the text. In these simulations, the VA current parameter λ_{VA} [see Eq. (5.1)] was set to be $3\sqrt{k}$, where k is the surface diffusion constant (see Sec. II). Also, we set $c = 3/4$ and $b = 2$, yielding, $a_+ = -0.11$ and $a_- = 0.47$. With these values, from our simulations we find $a_3 = 0.05$ $a_2 = 0.5$ $a_1 = 0.225$ $a_0 = 0.35$. For comparison, in the lower panel we include also the results obtained with $\lambda_{VA} = 0$ (solid lines)

data of Ref. [9] are also in accord with the predictions coming from our theory provided the VA is incorporated into the modeling. Practically significant among those data are the experimentally obtained in Ref. [9] surface diffraction patterns, i.e. the in-phase and out-of-phase diffraction patterns corresponding, respectively, to the surface Fourier transforms (FT) magnitude and slope distribution (SD) obtained here from our simulations. Here we show that these electron diffraction experimental data can be all explained by using our theory. Moreover, we make detailed predictions on the underlying surface morphology, which can be only partially guessed from the experimental diffraction data. Indeed, interestingly, due to the lack of the information on the scattered wave phase, two qualitatively different surface morphologies may have qualitatively the same form of Fourier transform magnitudes, i.e., the in-phase diffraction patterns. This peculiarity happens to be indeed important for the discussions of the aforementioned experiments on the Ag(110) growth in Ref [9]. Indeed, the FT magnitude pattern, seen in the intermediary regime of the transition on Ag(110) surface, turns out to be the same as that of the *RhP* state, (which is indeed realized in ripple rotation transition on Cu(110) and Rh(110) [13], see Sec. IV here). Still, the additional information on the Ag(110) intermediary state, coming from the experimental out-of-phase diffraction data, i.e., the facet slope distribution [9], suggests the presence of rectangular shape mounds similar to the roof-like pyramids of our Rectangular Rippled $R^{(rec)}$ states discussed in our previous sections. However, for zero VA the interface state we obtained at the very $R_1^{(rec)}$ -to- $R_2^{(rec)}$ transition has the FT with four peaks at the wave vector $(\pm q_1, \pm q_2)$, see Fig. 11. This is in contrast to the experiments on Ag(110) growth, indicating a *RhP* like FT pattern, with

two pairs of peaks, $(\pm q_1, 0)$ and $(0, \pm q_2)$, that are along the principal axes of the (110) surface, [9]. Here, we show that this experimental finding on the interface behavior on Ag(110) surface can be understood only by invoking the VA of the epitaxial growth. Furthermore, we elucidate the physical origin of these diffraction data in terms of some new and interesting interface morphologies that are all induced purely by the VA.

Within the continuum modeling, the VA affects the form of the surface curvature current in Eq. (2.2) by contributing to it terms which are *even* under vertical reflection $h \rightarrow -h$. For zero VA, the curvature current would have the simple Mullins form [see Eq. (2.3) and the discussion]. The Mullins current $\sim -\nabla(\Delta h)$ is *odd* with respect to the up-down vertical reflection $h \rightarrow -h$. Thus, this current does not break the (artificial) up-down symmetry, i.e., it does not introduce any VA. Likewise, under the vertical reflection, the surface non-equilibrium current $\vec{J}^{(NE)}(\vec{M})$ can be also shown to be odd for the surfaces possessing center of symmetry [due to the fact that $\vec{J}^{(NE)}(-\vec{M}) = -\vec{J}^{(NE)}(\vec{M})$, see Eq. (2.9)]. So, this current also does not introduce any VA. Due to this, the VA may affect only the higher derivative, curvature currents in Eq. (2.2). To the leading order, the VA emerges through the Villain current [6], of the form

$$J_{VA} = \frac{\lambda_{VA}}{2} \nabla(\nabla h)^2, \quad (5.1)$$

which is even under $h \rightarrow -h$ and thus breaks the artificial vertical reflection $h \rightarrow -h$ invariance of the interface dynamics Eq. (2.1). The VA current in Eq. (5.1) contributes the so-called conservative KPZ term $\sim -\nabla^2(\nabla h)^2$ to the interface velocity in Eq. (2.1). In the following, we examine the effects of the VA current Eq. (5.1) on the kinetic phase transition between the Rectangular Rippled states.

Our results on these effects are given in the figures 17 through 20. As discussed above, the VA current is a curvature current vanishing on flat facets [see Eq. (5.1)]. Thus, the VA does not affect the magnitudes of the selected slopes of the flat facets R_1 and R_2 in Eqs. (3.1) and (3.2), which are depicted in Fig. 17(a). Nonetheless, the VA does qualitatively affect the interface morphology in the transition region, as well as the interface data such as the SD and FT (compare Figs. 18 and 19 where $VA \neq 0$, with the previous Fig. 11 where $VA = 0$). In addition, the VA produces a huge enhancement of the interface roughness seen in Fig. 17(b) in the proximity of the transition between the two Rectangular Rippled states. Interestingly, close to the point corresponding to the maximum roughness, the interface structures itself into nearly square-like pyramids that are arranged side-by-side, see Figs. 18(d) and (e). It is noteworthy that similar side-by-side arranged mounds are seen in the kinetic Monte Carlo simulations of a qualitatively different system, namely the Ag(001) surface, [12]. For the present, less symmetric (110) surface, these side-by-side arranged pyramids are only approximately square shaped, see Fig. 18(d). They emerge due to a VA induced instability which we find active only in the transition region. It breaks the long roof-like pyramids of the $R_1^{(rec)}$ state into arrays of smaller four sided pyramids with no roof-like edges. On the other hand, the shapes of the long roof-like *pits* (inverted rooftops) are *not* affected by the VA at the transition, see Fig. 18(d) at $a = a_1$. At this point, our simulations yield the SD with equal probabilities of R_1 and R_2 facets [see Fig. 19(d) exhibiting SD with the R_1 and R_2 peak pairs of nearly equal magnitude at $a = a_1$]. It would be thus tempting to identify this particular value of a , obtained from slope distribution data, as the critical point value for the ripple rotation transition. This identification however turns put to be too simplistic, as evidenced by the

Fig. 18. Effects of the VA on the interface morphology (given here by surface contour plots) across the transition from $R_2^{(rec)}$ to $R_1^{(rec)}$ state. (a) The $R_2^{(rec)}$ state, with a disordered checkerboard arrangements of rectangular pyramids and pits. (b) An altered form of $R_2^{(rec)}$ state. Note that the rectangular pit sizes are depressed and that arrays of small rounded mounds form along rooftop like pyramids [see also Fig. 20(a)]. (c) Interface morphology at the point where FT exhibits four peaks of equal magnitude [see also Figs. 19(c) and 20(b)]. Interface structures itself into rectangular mounds packed side-by-side. (d) Interface morphology at the point where surface SD exhibits four peaks of equal magnitude [see also Fig. 19(d) and 20(c)]. It is an altered form of the $R_1^{(rec)}$ state with roof-top like pyramids replaced by arrays of nearly square shaped four-sided pyramids packed between longer in size pits (inverted roof-tops). As documented in (e), such a state develops throughout the parameter range where the enhanced roughening occurs (see Fig. 17). (f) The $R_1^{(rec)}$ state of roof-top like pyramids and pits

Fig. 19. Effects of the VA on the surface slope distributions (SD), i.e., out-of-phase diffraction patterns, and the surface Fourier transforms (FT), i.e., in-phase diffraction patterns, across the transition from the $R_2^{(rec)}$ to $R_1^{(rec)}$ state. Panels here directly correspond to the interface morphologies given in the panels of Fig. 18. Note that FT undergoes a transition in the panel (c) at $a = a_2$, whereas SD undergoes this transition in panel (d) at $a = a_1$.

surface FT, i.e., the in-phase diffraction pattern, which at $a = a_1$ turns out to still exhibit just one pair of peaks at $(\pm q_1, 0)$, like in the $R_1^{(rec)}$ state, see Fig. 19(d). This peculiarity is due to aforementioned feature of the long roof-like pits. They are not significantly affected by the VA and continue to grow in length along the x_2 -direction. Small square-like pyramids in Fig. 18(d) are packed between these long pits. This conspires to produce an $R_1^{(rec)}$ -like in-phase diffraction pattern with a single pair of peaks at $(\pm q_1, 0)$. Thus, at $a = a_1$ one has a transition point that is visible only in terms of the slope distributions, i.e., *out-of-phase* diffraction data that exhibit both R_1 and R_2 pairs of peaks with nearly equal magnitude. On the other hand, the interface Fourier transforms, i.e., the *in-phase* diffraction data exhibit a transition at a different (slightly smaller) value of $a = a_2$, see Fig. 19(c). For this particular value of a , the surface FT magnitude exhibits two pairs of peaks, at $(\pm q_1, 0)$ and $(0, \pm q_2)$ with nearly equal magnitude. This is documented in our figures 19 and 20 that strikingly reproduce the sequence of the FT changes experimentally observed in the ripple rotation on the Ag(110) in Ref. [9]. Interestingly, the presence of two pairs of FT peaks with nearly equal magnitudes, we find for $a \approx a_2$, off the point with maximum roughness occurring at $a \approx a_1$ where the SD exhibits two pairs of peaks with nearly equal magnitude and the nearly square shaped pyramids sitting side-by-side develop [see Fig. 18(d)]. On the other hand, for $a \approx a_2$, where the FT develops two pairs of peaks with nearly equal magnitudes, the interface structures itself into rectangular mounds (still) sitting side-by-side, see Fig. 18(c). This interface morphology is qualitatively different from the checker-board arrangement of rectangular pyramids and pits occurring in the $R_2^{(rec)}$ state that is present at smaller values of the

Fig. 20. 3d views of the real-space interface morphology and the corresponding FTs, i.e., in-phase diffraction patterns, for a non-zero VA, at several successive points along the transition between the rectangular rippled states. In Fig. (a), the altered form of the $R_2^{(rec)}$ state is shown. In it, pit size is suppressed whereas arrays of small mounds form along roof-tops. Note that this structure yields a FT essentially the same as that of the $R_1^{(rec)}$ state, with just two peaks at $(0, \pm q_2)$ [see, also, Fig. 19(a) and (b)]. In Fig. (b), the FT forms with two pairs of peaks, at $(\pm q_1, 0)$ and $(0, \pm q_2)$, having nearly equal magnitudes. This corresponds to the transition at $a = a_2$ discussed in the text. At it, the interface structures itself into rectangular pyramid sitting side-by-side [see also Fig. 18(c)]. In Fig. (c) the altered form of the $R_1^{(rec)}$ state is shown, with rooftop edges replaced by arrays of nearly square shaped four-sided pyramids [see also Fig. 18(d)]. Nonetheless, this complex structure has qualitatively the same FT as $R_1^{(rec)}$, with just two peaks at $(\pm q_1, 0)$ [see also Fig. 19(d)].

parameter a in Figs. 17 and 18 (see our discussions in the following).

To summarize our findings on the VA effect on the ripple rotation transition between the Rectangular Ripple states: VA introduces a sharp rise of the interface roughness yielding the prominent peak of the interface width seen across the transition in Fig. 17 from our simulations. We stress that such enhanced surface roughening has been indeed seen in the ripple rotation transition of Ag(110), in the epitaxial erosion experiments of Ref. [10]. The ripple rotation proceeds as a sequence of two experimentally interesting (for the diffraction surface probes) transitions that we find in the proximity of the surface roughness maximum. The first of them, at $a = a_1$, occurs close to the point of maximum roughness. This transition is experimentally detectable by means of out-of-phase diffraction patterns, i.e., interface slope distribution which for $a = a_1$ exhibits two pairs of equally strong peaks: the R_1 peaks at $(\pm M_1, 0)$ and the R_2 peaks at $(0, \pm M_2)$, seen in Fig. 19(d), at $a = a_1$. At this transition point, interface structures itself into nearly square shaped pyramids sitting side by side. These square-like pyramids form arrays that are packed between long roof-like pits. This fact conspires to produce an in-phase diffraction pattern, i.e., interface FT, which is for $a = a_1$ indistinguishable from that form the nearby rippled rectangular state $R_1^{(rec)}$, see Figs. 19(d) and 20(c). Thus, this first transition point, at $a = a_1$, can be seen only in the out-of-phase diffraction data. On the other hand, the in-phase diffraction data undergo a qualitative change at the second phase transition that is located at $a = a_2$, off the point with maximum roughness, see Fig. 17 and Fig. 19(c). At this transition, the in-phase diffraction pattern, i.e., interface FT magnitude plot exhibits two pairs of equally strong

peaks seen in Figs. 19(c) and 20(b): the R_1 -state-like peak at $(\pm q_1, 0)$ and the R_2 -state-like peak at $(0, \pm q_2)$. At this transition point, the surface structures itself into rectangular pyramids sitting side-by-side; see Fig. 18(c) and 20(b), both at $a = a_2$. Thus, by means of the standard experimental diffraction techniques, one can identify two transition points: (i) The out-of-phase diffraction transition point exhibiting four peaks in the slope distribution, occurring at $a = a_1$ [with $a_1 = 0.225$ in the simulations presented here in Figs. 17 through 20], and, (ii) The in-phase diffraction transition point exhibiting four peaks in the interface Fourier transform, occurring at $a = a_2$ [with $a_2 = 0.2$ in the simulations presented here].

Our simulations however indicate the existence of additional transitions and non-trivial surface morphologies that may not be easily detectable by means of the standard surface diffraction techniques, such as in- and out-of-phase diffraction patterns. We detail on these interesting VA induced phenomena hereafter. Thus, for the parameter a in the range $a_3 < a < a_2$ (with $a_3 \approx 0.05$ in our simulation) we find an interface state close in character but still different from the $R_2^{(rec)}$ rippled state, see Fig. 18(b). Prominent feature of this novel intermediary state are: (i) The VA induces a significant asymmetry between the elongated (“rectangular”) pyramids and the rectangular pits (inverted roof-tops). For $VA = 0$ both of them are of the same length. With $VA \neq 0$, however, the rectangular pits are significantly shorter than the elongated pyramids, as seen in Figs. 18(b) and 20(a). (ii) In addition, the VA induces an interesting instability of the rooftop edges on the elongated pyramids seen in Figs. 18(b) and 20(a). There, we see that the rooftop edges are actually replaced by arrays of small rounded mounds [see Figs. 18(b) and 20(a)]. These mounds are however small in size and thus do not qualitatively affect the interface diffraction

data, as documented in Figs. 19(b) and 20(a). A direct look at the interface, by means of STM images, would be thus needed to see these mounds in the experiments. Interestingly, these arrays of small mounds are seen to develop only on the rooftops of the elongated pyramids. There are no such arrays developing along the pits [see Fig. 18(b)].

Thus, for a in the range $a_3 < a < a_2$ in Fig. 17 [adjacent to the enhanced roughening range], we find a novel intermediary interface state, similar to the $R_2^{(rec)}$ state, but with highly reduced sizes of the rectangular pits, and with roof-top edges replaced by the arrays of VA induced small mounds. Importantly, this intermediary state does not exhibit an enhanced roughening [see Fig. 17], and, it has both the in-phase and out-of-phase diffraction patterns indistinguishable from those of the $R_2^{(rec)}$ state. Such a state can be thus discriminated from the $R_2^{(rec)}$ state only by real-space, STM images of the interface.

On the other side, for the parameter a in the range $a_2 < a < a_1$ in Fig. 17, we have the sharp increase of the interface roughness. It is accompanied with the earlier described non-trivial changes of the surface data such as its FT, i.e., the in-phase diffraction pattern that exhibits the four peaks at $a \approx a_2$, and, also, the changes of the surface SD, i.e., out-of-phase diffraction pattern that exhibits four peaks at $a \approx a_1$, close to the roughness maximum. As evidenced in Fig. 19, for $a < a_1$, both types of diffraction data are as in the $R_2^{(rec)}$ state, whereas, for $a > a_2$, both types of the diffraction data are as in the $R_1^{(rec)}$. Thus, in terms of the diffraction data, the ripple rotation transition actually occurs over an extended parameter range, $a_2 < a < a_1$. Our simulations indicate that this range may be narrow and characterized by a very steep rise of the interface roughness that actually

occurs between a_2 and a_1 , see Fig. 17. We emphasize that the interface states occurring on both sides of the extended transition range (a_2, a_1) are different from the standard Rippled Rectangular states. Thus, within the parameter a range (a_3, a_2) , we have the above described modified version of the $R_2^{(rec)}$ state, with reduced pit sizes and roof-top arrays of small rounded mounds, seen in Figs. 18(b) and 20(a). Likewise, within the a parameter range (a_1, a_0) in Fig. 17, we have the intensely rough interface state [Fig. 18(e)] that has the in-phase and out-of-phase diffraction data close to those of the $R_1^{(rec)}$ state. Yet, in the real space STM images, this state would resemble a square-pyramid structured interface, with the pyramids sitting side-by-side, as seen in Figs. 18(d) and (e), and 20(d). However, a careful look at the interface in Figs. 18(d) and (e) shows that this state has the long length-scale organization of the $R_1^{(rec)}$ state, however, with long roof-like rectangular mounds replaced by arrays of small four-sided pyramids packed between long rectangular pits. Due to this feature, this state exhibits the diffraction patterns which are qualitatively the same as that of the rectangular rippled state $R_1^{(rec)}$. Thus, the real space STM images are needed to discriminate this exotic, intensely rough pyramidal state, seen in Fig. 18(e), from the $R_1^{(rec)}$ state, seen in Fig. 18(f).

In summary, we have revealed here a wealth of interfacial phenomena that the VA produces in the ripple rotation transition between the rectangular rippled states $R_1^{(rec)}$ and $R_2^{(rec)}$. Across this transition, with the change of the temperature-like parameter a , there is number of interesting transitions occurring at the four characteristic points denoted here as a_3, a_2, a_1 , and a_0 ($a_3 < a_2 < a_1 < a_0$). In the range $a < a_3$, the ordinary $R_2^{(rec)}$ occurs. In the range $a_3 < a < a_2$, an altered form of the $R_2^{(rec)}$ occurs, with depressed pit sizes and with rooftop edges replaced by arrays of small rounded mounds. Still, all diffraction data

of this state are the same as those of the $R_2^{(rec)}$ state. At $a \approx a_2$, the interface structures itself as rectangular mounds sitting side-by-side, and the in-phase diffraction pattern exhibits two equally strong pairs of peaks, at $(\pm q_1, 0)$ and $(0, \pm q_2)$. The range $a_2 < a < a_1$ (characterized by a steep increase of the interface roughness) is an extended ripple rotation transition region inside of which the interface SD (out-of-phase diffraction pattern) is more like to that of $R_2^{(rec)}$ state, whereas the interface FT (the in-phase diffraction pattern) is more like to that of the $R_1^{(rec)}$ state. At $a \approx a_1$, the interface SD, i.e., out-of-phase diffraction pattern has two equally strong peaks, at $(\pm M_1, 0)$ and $(0, \pm M_2)$. For a in the range $a_1 < a < a_0$, an altered form of the $R_1^{(rec)}$ state occurs. It exhibits enhanced roughening and it is characterized by roof-top edges replaced by arrays of nearly square-shaped pyramids. Still, all diffraction data of this intensely rough state are essentially the same as those of the $R_1^{(rec)}$ state that occurs for $a > a_0$. Thus, in the experimental studies of the ripple rotation transition on (110) crystal surfaces, real space surface probes, such as STM images are needed to reveal the novel interfacial states revealed by our simulations in Figs. 18(e) and 18(b).

VI. Appendix A

In this appendix we present the stability analysis of the interface flat configurations (facets). It is important for the discussions presented in Sec III. To obtain stability conditions we expand the interface profile $h(\vec{x}, t)$ around the flat interface profile, with the slope $\vec{M}_0$,

$$h(\vec{x}, t) = \vec{M}_0 \vec{x} + \delta h(\vec{x}, t). \quad (\text{A1})$$

In terms of the interface slope $\vec{M} = \vec{\nabla} h$,

$$\vec{M} = \vec{M}_0 + \vec{\nabla} \delta h = \vec{M}_0 + \delta \vec{M}. \quad (\text{A2})$$

Our primary interest here is to analyze stability of the preferred facets, for which $\vec{J}^{NE}(\vec{M}_0) = \vec{0}$. We will employ the expansion in Eqs. (A1) and (A2) to study the facet stability in our model Eq. (2.17). For this purpose, we first expand the non-equilibrium current $\vec{J}^{NE}(\vec{M}) = [J_1(M_1, M_2), J_2(M_1, M_2)]$,

$$\vec{J}_\alpha^{NE}(\vec{M}_0 + \delta \vec{M}) = \vec{J}_\alpha^{NE}(\vec{M}_0) + \sum_{\beta=1}^2 \left. \frac{\partial J_\alpha^{NE}}{\partial M_\beta} \right|_{\vec{M}=\vec{M}_0} \delta M_\beta + \dots \quad (\text{A3})$$

Here $\alpha = 1, 2$. By Eqs. (A3) and (2.1),

$$\frac{\partial}{\partial t} \delta h = - \sum_{\alpha=1}^2 \frac{\partial}{\partial x_\alpha} \sum_{\beta=1}^2 \left. \frac{\partial J_\alpha^{NE}}{\partial M_\beta} \right|_{\vec{M}=\vec{M}_0} \delta M_\beta + \dots \quad (\text{A4})$$

The ellipses in Eq. (A4) include the terms nonlinear in $\delta \vec{M} = \vec{\nabla} \delta h$, and, also, higher order derivative terms, coming from the curvature current [see Eq. (2.3)]. Here, we perform the

linear stability analysis, so the nonlinear terms will be ignored. Also, the higher order derivative terms are subdominant in the long length scale (short wave vector) limit interesting for the stability of large facets. It is assumed that these higher order terms [such as the surface diffusion term Eq. (2.3)] are stabilizing, i.e., that there are no short length scale instabilities. Thus, the facet instability may emerge only at long length scales, from the terms exposed in Eq. (A4), which are purely due to the surface non-equilibrium current. Using

$$\frac{\partial}{\partial x_\alpha} \delta M_\beta = \frac{\partial}{\partial x_\beta} \delta M_\alpha = \frac{\partial^2}{\partial x_\alpha \partial x_\beta} \delta h, \quad (\text{A5})$$

Eq. (A4) can be shown to be equivalent to

$$\frac{\partial}{\partial t} \delta h = - \sum_{\alpha=1}^2 \sum_{\beta=1}^2 \frac{1}{2} \left(\frac{\partial J_\alpha}{\partial M_\beta} + \frac{\partial J_\beta}{\partial M_\alpha} \right)_{\vec{M}=\vec{M}_0} \frac{\partial^2}{\partial x_\alpha \partial x_\beta} \delta h. \quad (\text{A6})$$

Eq. (A6) permits the solution of the form

$$\delta h(\vec{x}, t) \sim \exp[\omega(q_1, q_2)t] \cdot \exp[iq_1 x_1 + iq_2 x_2], \quad (\text{A7})$$

with $\omega(q_1, q_2)$, the dispersion relation, given by

$$\omega(q_1, q_2) = - \left(T_{11} q_1^2 + 2T_{12} q_1 q_2 + T_{22} q_2^2 \right). \quad (\text{A8})$$

Here,

$$T_{\alpha\beta} = T_{\beta\alpha} = - \frac{1}{2} \left(\frac{\partial J_\alpha}{\partial M_\beta} + \frac{\partial J_\beta}{\partial M_\alpha} \right). \quad (\text{A9})$$

For a stable facet, $\omega(q_1, q_2)$ in Eq. (A8) must be negative for *any* (q_1, q_2) , thus the matrix

$T_{\alpha\beta}$ must be positively definite (PD). We note that for the special case when the

dynamics is governed by an effective free energy, the current $\vec{J}^{NE}(\vec{M}) = -\partial U / \partial \vec{M}$ [see Eq. (2.12a)], and thus by Eq. (A9),

$$T_{\alpha\beta} = \frac{\partial^2 U}{\partial M_\alpha \partial M_\beta} . \quad (\text{A10})$$

For this case, the preferred slopes with $\vec{J}^{NE}(\vec{M}_0) = \vec{0}$ are simply minima of the potential $U(\vec{M})$, and the absolute minima dominate at long times [see Eq. (3.10) and the discussion]. The selected facets simply correspond to the absolute minimum of $U(\vec{M})$, which is assured to be stable, i.e., the stability matrix (A10) must be PD. Thus, for this case, it is obviously assured that at least one zero of $\vec{J}^{NE}(\vec{M})$ is stable, i.e., it is impossible that all zeros of $\vec{J}^{NE}(\vec{M})$ are unstable. On the other hand, for the interface dynamics that is not governed by an effective free energy, the situation with all zeros of $\vec{J}^{NE}(\vec{M})$ being unstable is, in general, possible. For example, for the general case of our model Eq. (2.17), with $c \neq 0$, there is no an effective free energy generating dynamics, and, in a range of the parameter space, the situation with all zeros unstable is indeed realized. This is exemplified by the following discussions, which indeed reveal such a parameter range existing only for $c \neq 0$. It corresponds to the range in which the unusual Buckled Rippled phase occurs.

We proceed with our stability analysis of facets yielding the kinetic phase diagram in Fig. 3. For our model Eq. (2.17), the stability matrix (A9) has the form:

$$\begin{aligned} T_{11}(\vec{M}) &= -(1+a) + 3M_1^2 + (b+c)M_2^2 \\ T_{12}(\vec{M}) &= T_{21}(\vec{M}) = bM_1M_2 \\ T_{22}(\vec{M}) &= -(1-a) + 3M_2^2 + (b-c)M_1^2 \end{aligned} \quad (\text{A11})$$

Let us analyze the stability of various types of zeros of $\vec{J}^{NE}(\vec{M})$ introduced in Sec. III.

Singlet ($M_1 = M_2 = 0$)

For the singlet, by Eqs. (A11) and (A8) we find the dispersion relation

$$\omega_{\text{sin}}(\vec{q}) = q_1^2(1+a) + q_2^2(1-a) . \quad (\text{A12})$$

By Eq. (A12), for any a there are some values of $\vec{q}$ such that $\omega_{\text{sin}}(\vec{q}) > 0$. Thus, the singlet is generally unstable.

R₁ doublet ($M_1 \neq 0, M_2 = 0$)

By Eq. (3.1), this doublet exists only for $1+a > 0$. Using Eqs. (3.1), (A11), and (A8) we find the dispersion relation for the R_1 doublet,

$$\omega_{R_1}(\vec{q}) = -2q_1^2(1+a) - q_2^2(1+b-c)[a - a_+(b,c)] . \quad (\text{A13})$$

Here, $a_+(b,c)$ is given by Eq. (3.4). By Eq. (A13), for $1+b-c > 0$, the R_1 is unstable for $a < a_+(b,c)$ and stable for $a > a_+(b,c)$.

R₂ doublet ($M_1 = 0, M_2 \neq 0$)

By Eq. (3.1), this doublet exists only for $1-a > 0$. Using Eqs. (3.2), (A11), and (A8) we find the dispersion relation for the R_2 doublet,

$$\omega_{R_2}(\vec{q}) = -2q_2^2(1-a) - q_1^2(1+b+c)[a_-(b,c) - a] . \quad (\text{A14})$$

Here, $a_-(b,c)$ is given by Eq. (3.4). By Eq. (A14), for $1+b+c > 0$, the R_2 is unstable for $a > a_-(b,c)$ and stable for $a < a_-(b,c)$.

Quartet ($M_1 \neq 0, M_2 \neq 0$)

For the quartet, M_1 and M_2 are as in Eq. (3.3), which can be used to show that the quartet zero exists only between the lines a_+ and a_- in Fig. 3. Using Eqs. (3.3), (A11), (A8) we find the dispersion relation for the quartet

$$\omega_{quart}(\vec{q}) = -2q_1^2 M_1^2 - 2q_2^2 M_2^2 - 4bq_1 q_2 M_1 M_2. \quad (\text{A15})$$

By denoting $Q_1 = q_1 M_1$, and $Q_2 = q_2 M_2$, Eq. (A15) reduces to

$$\omega_{quart} = -2Q_1^2 \left[\left(\frac{Q_2}{Q_1} + b \right)^2 + 1 - b^2 \right]. \quad (\text{A16})$$

By Eq. (A16), the quartet becomes unstable for $b > 1$ in the phase diagram in Fig. 3. By the above discussions, for b in the range $1 < b < b_x = \sqrt{1+c^2}$ and a between a_+ and a_- , all zeros of $\vec{J}^{NE}(\vec{M})$ are unstable. In this region the interface can not develop large facets corresponding to any of the zeros of $\vec{J}^{NE}(\vec{M})$. Rather, the interface structures that carry persistent surface currents develop, as documented by our simulations in Sec. IV.

VII. Appendix B

In this Appendix, we consider problem of the existence of static edges between two facets with slope vectors $\vec{M}_A$ and $\vec{M}_B$, see Fig. 21(a). These two vectors are assumed to be preferred, i.e., that they vanish the non-equilibrium current, $\vec{J}^{NE}(\vec{M}_A) = \vec{0}$ and $\vec{J}^{NE}(\vec{M}_B) = \vec{0}$. First, we will consider the model Eq. (2.1) with general form of the non-equilibrium current, whereas the curvature current is, as in Sec. II, assumed to be of the surface diffusion type. For this model we will show here that the static edge exists provided the line integral

$$\int_{\vec{M}_A}^{\vec{M}_B} d\vec{M} \cdot \vec{J}^{NE}(\vec{M}) = 0. \quad (\text{B1})$$

Here, the integral goes, in the M -space, along the straight line joining the vectors $\vec{M}_A$ and $\vec{M}_B$, see Fig. 21(a). We will use Eq. (B1) to derive Eq. (3.9) giving the critical value a_{cr} at the $R_1^{(rec)}$ -to- $R_2^{(rec)}$ phase transition. Let us first prove the condition in Eq. (B1). For this purpose we note that there is a natural coordinate system associated with an edge: Indeed, along an edge the two facets intersect, so $\vec{M}_A \cdot \vec{x} = \vec{M}_B \cdot \vec{x}$. By noting that $\vec{x} = |\vec{x}| \hat{e}$, where $\hat{e}$ is the unit vector along the edge, we find that $\vec{M}_A \cdot \hat{e} = \vec{M}_B \cdot \hat{e}$, see Fig. 21(a). This relation actually determines $\hat{e}$ for a given $\vec{M}_A$ and $\vec{M}_B$. Let us denote by $\hat{t}$ the unit vector perpendicular to $\hat{e}$, $\hat{t} \cdot \hat{e} = 0$, and let us employ the Cartesian coordinate system associated with unit vectors $\hat{e}$ and $\hat{t}$. Thus, we change the in-plane coordinates as

Fig. 21: The figure (a) aids the derivation of Eq. (B1), that gives the condition for the coexistence of nonequivalent facets across a static edge [see the Appendix B text for details]. The condition is a generalization of the usual Gibbs condition to the far from equilibrium transitions in systems with no effective free energy description available. The figure (b) depicts the integration path used in Eq. (B14) to derive Eq. (3.9) that gives the transition line between the two Rectangular Rippled states $R_1^{(rec)}$ and $R_2^{(rec)}$ in the kinetic phase diagram in Figs. 3 and 4.

$$\vec{x} = x_1 \hat{i}_1 + x_2 \hat{i}_2 = x_L \hat{e} + x_T \hat{t} \quad (\text{B2})$$

where (x_1, x_2) are the original coordinates (say, as in Sec. II), whereas x_L and x_T , are, respectively, the longitudinal (along the edge) and perpendicular (to the edge) coordinate. It will be convenient to express the vectors $\vec{M}$ and $\vec{J}^{NE}$ using these “edge” coordinates, via

$$\begin{aligned} \vec{M} &= M_1 \hat{i}_1 + M_2 \hat{i}_2 = M_L \hat{e} + M_T \hat{t}, \\ \vec{J} &= J_1^{(NE)} \hat{i}_1 + J_2^{(NE)} \hat{i}_2 = J_L^{(NE)} \hat{e} + J_T^{(NE)} \hat{t}, \end{aligned} \quad (\text{B3})$$

see Fig. 21(a). We note that this change of coordinates is a rotation, preserving the form of the 2-d divergence,

$$\vec{\nabla} \cdot \vec{J}^{(NE)} = \frac{\partial J_1^{(NE)}}{\partial x_1} + \frac{\partial J_2^{(NE)}}{\partial x_2} = \frac{\partial J_L^{(NE)}}{\partial x_L} + \frac{\partial J_T^{(NE)}}{\partial x_T}. \quad (\text{B4})$$

For the infinitely long edge, the interface profile has the form

$$h(\vec{x}) = x_L M_e + \psi(x_T), \quad (\text{B5})$$

see the contour lines in Fig. 21(a). The corresponding slope vector components are

$$\begin{aligned} M_L &= \frac{\partial h}{\partial x_L} = M_e = \text{const.}, \\ M_T &= \frac{\partial h}{\partial x_T} = M_T(x_T) = \frac{d\psi(x_T)}{dx_T}, \end{aligned} \quad (\text{B6})$$

i.e., $M_L = \vec{M} \cdot \hat{e}$ is just a constant, whereas $M_T(x_T) = \vec{M} \cdot \hat{t}$ is a function of x_T only. An edge is like a domain wall in a magnetic system, with the slope

$$\vec{M}(x_T) = M_e \hat{e} + M_T(x_T) \hat{t}, \quad (\text{B7})$$

approaching $\vec{M}_A$ for $x_T \rightarrow -\infty$, and $\vec{M}_B$ for $x_T \rightarrow +\infty$. To discuss the form of $M_T(x_T)$, note that $\vec{J}^{NE}(\vec{M})$, by Eq. (B7), depends on x_T only. Thus, by Eq. (B4)

$$\vec{\nabla} \vec{J}^{NE} = \frac{d\vec{J}^{NE}}{dx_T} = \frac{d}{dx_T} (\hat{t} \cdot \vec{J}^{NE}(\vec{M})) \quad (\text{B8})$$

For the static edge, $\partial h / \partial t = 0$, and by Eqs. (2.17), (B6), and (B8), we find

$$0 = \frac{d}{dx_T} (\hat{t} \cdot \vec{J}^{NE}) - k_T \left(\frac{d}{dx_T} \right)^4 \psi(x_T), \quad (\text{B9})$$

where k_T is a linear combination of the constants $k_{\alpha\beta}$ in Eq. (2.17a). By Eqs. (B9) and (B6), one can easily see that

$$-\hat{t} \cdot \vec{J}^{NE}(\vec{M}) - k_T \frac{d^2 M_T(x_T)}{dx_T^2} = \text{const} = 0. \quad (\text{B10})$$

The *const* on the right-hand side here must be set to zero, because for $x_\perp \rightarrow \pm\infty$, the non-equilibrium current vanishes at the preferred slopes $\vec{M}_A$ and $\vec{M}_B$ that are asymptotically reached in these limits. It is illuminating to note that Eq. (B10) is isomorphic to that of the Newtonian dynamics of a particle with the mass k_T and the position $M_T(x_T)$ versus time x_T , moving under the force $\sim \hat{t} \cdot \vec{J}^{NE}(\vec{M})$. For the edge type solution, the particle kinetic energy $\sim \left(\frac{dM_T}{dx_T} \right)^2$ approaches zero in the limits $x_T \rightarrow -\infty$ and $x_T \rightarrow +\infty$, in which $\vec{M}_T \rightarrow (\vec{M}_A)_T$ and $\vec{M}_T \rightarrow (\vec{M}_B)_T$, respectively, see Fig. 21(a). It follows that the total work of the force $\sim \hat{t} \cdot \vec{J}^{NE}(\vec{M})$ along this displacement is zero,

$$\int_{(\vec{M}_A)_r}^{(\vec{M}_B)_r} d\vec{M}_T (\hat{t} \cdot \vec{J}(\vec{M})) = 0. \quad (\text{B11})$$

By Eq. (B7), one can see that Eq. (B11) is equivalent to Eq. (B1), with the integration path in the M -space being the straight line joining the facet vectors $\vec{M}_A$ and $\vec{M}_B$. This completes our proof of the edge existence condition in Eq. (B1).

For the special cases with the non-equilibrium current generated by a potential $U(\vec{M})$, $\vec{J}^{NE} = -\partial U(\vec{M})/\partial \vec{M}$ (see Sec. II), the Eq. (B1) reduces to the simple condition $U(\vec{M}_A) = U(\vec{M}_B)$. In terms of the effective free energy concept, this is analogous to the standard Gibbs condition of free energy density equality at the first order transitions between two different phases. However in general, as discussed in Sec. II, the effective free energy may exist here only under special circumstances, that is, if the parameter c in the model Eq. (2.17) vanishes. Thus, to discuss the general situation with $c \neq 0$, we must resort to the more general condition for the static edge existence stated in Eq. (B1). Since, in general, $\vec{J}^{NE}(\vec{M})$ is *not* a gradient of a potential, the value of the line integral in Eq. (B1) depends on the path joining $\vec{M}_A$ and $\vec{M}_B$. As discussed above, the proper path here is the straight line joining $\vec{M}_A$ and $\vec{M}_B$ in the M -space.

If the facet slopes $\vec{M}_A$ and $\vec{M}_B$ are two equivalent vectors (related by the surface symmetry operation) then, by invoking the current symmetries in Eqs. (2.6)-(2.9), the condition Eq. (B1) can be easily shown to be satisfied. Thus, say, the two facets of R_1 doublets can always form static edges (seen in the R_1 rippled phase). Likewise, the facets of the quartets can always form static edges (seen in the Rhomboidal pyramids phase).

However, a strikingly different situation occurs for the static edges formed by two non-equivalent facets with slope vectors $\vec{M}_A$ and $\vec{M}_B$. In this case, the static edge existence condition can be satisfied only for special (critical) values of system parameters. Significant example here is the static edge between one of R_1 facets, with the slope vector

$$\vec{M}_A = \left(\sqrt{1+a}, 0 \right) \quad (\text{B12})$$

and one of the R_2 facets, with the slope vector

$$\vec{M}_B = \left(0, \sqrt{1-a} \right), \quad (\text{B13})$$

see Eqs. (3.1) and (3.2), and Fig. 21(b). These two facets can coexist along a static edge only under special conditions. Indeed, by performing the line integral in Eq. (B1), along the straight line joining $\vec{M}_A$ in Eq. (B12), with $\vec{M}_B$ in Eq. (B13), for $\vec{J}^{NE}(\vec{M})$ as in Eq. (2.16b) [see Fig. 21(b)], we find that Eq. (B.1) reduces to

$$\int_{\vec{M}_A}^{\vec{M}_B} d\vec{M} \cdot \vec{J}^{NE}(\vec{M}) = -a + \frac{1}{6}c(1-a^2) = 0. \quad (\text{B14})$$

Solving the quadratic equation in Eq. (B14) yields the critical value of the parameter a . This critical value a_{cr} is the one stated in Eq. (3.9). Of the two solutions of the quadratic equation (B14), only the one with $|a| < 1$ is appropriate [see Eqs. (B12) and (B13)].

For the special case $c = 0$, the non-equilibrium current in Eq. (2.16b) is derivable from a potential $U(M_1, M_2)$, via $J_1 = -\partial U / \partial M_1$ and $J_2 = -\partial U / \partial M_2$, with

$$U(M_1, M_2) = -\frac{1+a}{2}M_1^2 - \frac{1-a}{2}M_2^2 + \frac{1}{4}M_1^4 + \frac{b}{2}M_1^2M_2^2 + \frac{1}{4}M_2^4 \quad (\text{B15})$$

For $a = 0$ and any $b > 1$, this potential has two degenerate minima at the slope vectors $\vec{M}_A = (1, 0)$ and $\vec{M}_B = (0, 1)$. This is in accord with Eq. (3.9), which predicts that $a_{cr} = 0$ for $c \rightarrow 0$. At this point, $\vec{M}_A$ and $\vec{M}_B$ facet coexist and this gives rise to the formation of a four-sided pyramidal phase at this critical point. On the other side, a small positive a breaks this degeneracy in favor of the $\vec{M}_A$ facet, Eq. (B12), that have smaller effective free energy density (B15) than the $\vec{M}_B$ facet, Eq. (B13). This gives rise to the formation of the $R_1^{(rec)}$ phase, with the dominant $\vec{M}_A$, i.e., R_1 facets outgrowing smaller, less rapidly growing $\vec{M}_B$, i.e., R_2 facets. For a similar reason, for $a < 0$, the $R_2^{(rec)}$ phase is favored, with the dominant R_2 facets outgrowing smaller, less rapidly growing R_1 facets. All these trends can be easily understood in terms of the effective free energy, i.e., the potential (B15) that exist for $c = 0$, and ensures that the phase transition is governed by the free energy minimization [see Eq. (3.10) and the discussion there]. It is however remarkable that a similar first order transition phenomenon occurs for $c \neq 0$ as well, in the absence of an exact effective free energy. For this case, there is just a shift of the critical value a_{cr} from zero to the nonzero value given by Eq. (3.9).

Finally, we recall that the condition Eq. (B1) applies for the curvature currents of the surface diffusion form. Here, we have set to zero the vertical asymmetry curvature currents, such as the Villan current $\sim -\vec{\nabla}(\vec{\nabla}h)^2$ [4,5]. Such currents can be also discussed along the above lines, and the resulting conditions generalizing (B1) can be derived. We are not going to detail on them here, but only remark that the critical values of the parameters such as a_{cr} in Eq. (3.9) are affected by the strength of the vertical asymmetry [17]. We have revealed this effect also by simulations of $R_1^{(rec)}$ and $R_2^{(rec)}$ phases [17]. We

note that, in contrast to $R_1^{(rec)}$ -to- $R_2^{(rec)}$ transition, all other transitions in the phase diagram in Figs. 3 and 4, are not affected by the strength of the vertical asymmetry.

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Chapter 3

DISLOCATION DYNAMICS AND COARSENING OF RIPPLED STATES ON (110) SURFACES

I. INTRODUCTION

In this Chapter we develop an analytic framework for understanding the interface dynamics of the rippled states on (110) surfaces. The simulations of the Chapter 2 of this thesis evidence the prominent role of topological defects - the moving dislocations disordering the periodic order of various interfacial states. In Sec. II of this Chapter, we derive the basic laws of the dislocation dynamics, which relates dislocation velocities to the interfacial length scales such as the period λ of the rippled state. Next, in Sec. III, we use these laws to derive the interface coarsening laws and analytically explain the results of our simulations in Chapter 2.

II. KINETIC THEORY OF THE DISLOCATION DYNAMICS IN RIPPLED STATES ON (110) SURFACES

Basic structure of a single dislocation, close to its core is shown in Fig. 1, for the case of the R_2 rippled state. The dislocation in the figure 1(b) moves to the right. As discussed in Chapter 2, this dislocation motion is essential for the overall interface dynamics. It is the primary mechanism of the interfacial coarsening: As the dislocation in Fig. 1 moves, the two facets of the width λ (above and below the middle facet) merge to form the larger facet of the width 2λ . In this section, we address the structure and dynamics of these dislocations. In particular, we reveal the law relating the dislocation velocity to the phase period, $v(\lambda)$. This law is essential for obtaining the interface coarsening laws, pursued in Sec. III of this Chapter.

As the first step in this direction, we elucidate the dislocation core geometry in Fig. 1. It depicts a knife dislocation with symmetric edges pattern. For such a dislocation, the interface profile is anti-symmetric, $h(x_1, -x_2) = -h(x_1, x_2)$, in the coordinate system with the origin at the dislocation core in Fig. 1(b). In this figure, for $x_1 > 0$, the middle facet [for $|x_2| < u(x_1)$] is flat, i.e., it is an R_2 facet, with

$$h(x_1, x_2) = M_0 x_2, \quad (2.1)$$

whereas the facet above it is weakly curved in the core region, with the profile of the form,

$$h(x_1, x_2, t) = M_0 \frac{\lambda}{2} - M_0 \left(x_2 - \frac{\lambda}{2} \right) + \delta h(x_1, x_2, t). \quad (2.2)$$

Fig. 1. Interface profile [Fig. (a)] and the corresponding facet edges [Fig. (b)] in the vicinity of a knife type dislocations in the ordinary rippled state R_2 . The dislocation moves to the right in Fig. (b), see our text for details. ξ_c labels the lateral core size, along the direction of the dislocation motion

Here, $\delta h \rightarrow 0$ as $x_1 \rightarrow \infty$, so in this limit the edge between the middle and the upper facet is at $x_2 = \lambda/2$, see Fig. 1(b). The edge shape $u(x_1)$ [see Fig 1(b)] can be found as the intersection of the surfaces in Eqs. (2.1) and (2.2), yielding the equation

$$u(x_1, t) = \frac{\lambda}{2} + \frac{\delta h(x_1, x_2 = u(x_1, t), t)}{2M_0}. \quad (2.3)$$

For a given form of δh , at long times Eq. (2.3) can be solved for the edge shape $u(x_1, t)$. As discussed in the following, the dislocation core becomes sharp, at long times, with λ much smaller than the core lateral size ξ_c , in Fig. 1(b). Due to this, the x_2 -dependence of δh in Eq. (2.3) can be ignored. In the absence of the x_2 -dependence, the slope vector field on the upper facet in Fig. 1(b) is simply

$$M_1(x_1, t) = \frac{\partial}{\partial x_1} \delta h(x_1, t), \quad M_2 = -M_0, \quad (2.4)$$

whereas, by Eq. (2.3), the edge profile is directly found as

$$u(x_1, t) = \frac{\lambda}{2} + \frac{\delta h(x_1, t)}{2M_0}. \quad (2.5)$$

As, $\delta h(x_1, t) \rightarrow 0$ for $x_1 \rightarrow \infty$, one has $u(x_1, t) \rightarrow \lambda/2$ in this limit. On the other hand, by Fig. 1(b), $u(x_1, t)$ vanishes at the very core. So, by Eq. (2.5), $\delta h = -M_0 \lambda$ at the core. By using these facts and Eq. (2.4), we find,

$$\int_{x_c}^{\infty} dx_1 M_1(x_1, t) = M_0 \lambda, \quad (2.6)$$

for the core located at $x_1 = x_c$. Hereafter, we specialize to the steadily traveling interface profile, with the dislocation core traveling with constant velocity v . That is, the core

position $x_c = vt$, and $\delta h(x_1, t) = \delta h(x_1 - vt)$. Thus, also, $M_1(x_1, t) = M_1(x_1 - vt)$, whereas,

$$\frac{\partial}{\partial t} \delta h = -v \frac{\partial}{\partial x_1} \delta h = -v M_1. \quad (2.7)$$

Eqs. (2.7) and (2.4) can be combined with the interface dynamics law, given by Eq. (2.1) of Chapter 2, to obtain

$$-v M_1(x_1) = -\frac{d}{dx_1} J_1^{(NE)}(M_1(x_1), M_2 = M_0). \quad (2.8)$$

Eq. (2.8) is a differential equation that can be solved for the slope $M_1(x_1)$ of the upper, moving facet and, eventually, for the edge profile $u(x_1)$ in Fig 1. In the practically interesting limit $\xi_c \gg \lambda$, the curvature surface currents (see Sec. II of Chapter 2) can be ignored, as done in the equation (2.8) above. In this limit, the surface non-equilibrium current $\vec{J}^{NE}(\vec{M})$ plays the dominant role in determining the shape of the “traveling” facets, such as the upper and lower facets in Fig 1(b). In this figure, on the middle flat facet $\vec{J}^{NE} = 0$, whereas the upper and lower facets both move through a non zero downhill current that displaces the material from the upper facet (there, $\vec{J}^{NE}$ flows to the left in the figure) to the lower facet (there, $\vec{J}^{NE}$ flows to the right). Importantly, note that this removal of the material from the upper facet and its subsequent absorption on the lower facet causes the dislocation in Fig 1(b) to move to the right. To obtain the dislocation velocity v from this physical picture, we integrate Eq. (2.8) over the range $x_c < x_1 < \infty$, to obtain

$$\begin{aligned}
-v \int_{x_c}^{\infty} dx_1 M_1(x_1) &= -J_1^{NE}(M_1 = 0, M_2 = M_0) + J_1^{NE}(M_1 = M_1(0), M_2 = M_0) = \\
&= +J_1^{NE}(M_1 = M_1(x_c), M_2 = M_0) \quad ,
\end{aligned} \tag{2.9}$$

since the preferred R_2 slope ($M_1 = 0, M_2 = M_0$), with $\vec{J}^{NE} = 0$, is reached for $x_1 \rightarrow \infty$.

By Eqs. (2.9) and (2.6),

$$M_0 v \lambda = -J_1^{NE}(M_1(x_c), M_0). \tag{2.10}$$

For a given λ , equation (2.10) relates the dislocation velocity v to the slope component $M_1(x_c)$ of the upper facet at the core $x_1 = x_c$ in Fig. 1(b). $M_1(x_c)$ is directly related to the dislocation sharpness, i.e., its aspect ratio λ/ξ_c . Indeed, by Fig. 1(b), and Eq. (2.3),

$$\frac{\lambda/2}{\xi_c} \cong \frac{\partial u}{\partial x_1}(x_1 = x_c) = \frac{M_1(x_c)}{2M_0}, \tag{2.11}$$

Thus, the dislocation aspect ratio is

$$\frac{\lambda}{\xi_c} \cong \frac{M_1(x_c)}{M_0}. \tag{2.12}$$

Eq. (2.12) will be used in the following to show that the dislocation aspect ratio becomes small in the practically interesting limit of large λ [see Eq. (2.19b) in the following]. Due to this, as evidenced also by our simulation of Sec. IV in Chapter 2., the dislocations get sharper and sharper over the coarsening process. In addition to the dislocation motion, the interface coarsening involves also the processes of dislocations annihilations, as discussed in Sec. IV of Chapter 2. Due to the annihilations, at long times the dislocations ensemble becomes dilute. For dilute dislocation systems, it is sufficient to consider just a single dislocation system in order to obtain its velocity v and the aspect ratio $\lambda/\xi_c = M_1(x_c)/M_0$ as functions of λ . To accomplish this we need one more [in

addition to Eq. (2.10)] relation between these three fundamental characteristics of the traveling dislocations. This relation can be obtained by applying the equation (3.10) of Chapter 2 to the single dislocation system. In the single dislocation system, over the time dt , the total length of the two edges terminating at the dislocation core in Fig. 1(b) shortens by the length $dl = vdt$. This yields the change of the net effective free energy $dF_{eff} = -2\sigma dl = -2\sigma vdt$, with σ , the edge line tension (see Ref. [19] of Ch.1). Thus, by Eq. (3.10) of Chapter 2,

$$-2\sigma v = -\int dx_2 \int dx_1 \left(\frac{\partial h}{\partial t} \right)^2. \quad (2.13)$$

Here, $\partial h / \partial t \neq 0$ only on the surfaces of the upper and lower traveling facets in Fig 1(b).

These two facets [each of the width $\int dx_2 = \lambda$] equally contribute to the right hand side of Eq. (2.13), which thus reduces to,

$$-2\sigma v = -2\lambda \int_{x_c}^{\infty} dx_1 \left(\frac{\partial h}{\partial t} \right)^2.$$

Using here Eq. (2.7), we obtain,

$$\sigma v = \lambda \int_{x_c}^{\infty} dx_1 \left(v M_1(x_1) \right)^2. \quad (2.14)$$

Eqs. (2.14) and (2.10) constitute our two fundamental laws of the dislocation dynamics. We will use them here to obtain the dislocation velocity v and its aspect ratio $\lambda / \xi_c = M_1(x_c) / M_0$ as functions of λ , i.e., of the rippled state period. Prior to this we note that, as $M_1(x_1) \approx M_1(x_c)$ for $x_1 - x_c < \xi_c$ and $M_1(x_1) \approx 0$ for $x_1 - x_c > \xi_c$, the equation (2.14) implies the scaling relation $\sigma v \sim \lambda \xi_c v^2 (M_1(x_c))^2$. Thus,

$$v = \text{const.} \frac{\sigma}{\lambda \xi_c (M_1(x_c))^2}, \quad (2.15a)$$

so, by Eq. (2.12),

$$v = \text{const.} \frac{\sigma \xi_c}{(M_0)^3 \lambda^3} \sim \frac{\xi_c}{\lambda^3}. \quad (2.15b)$$

Eq. (2.15b) can be easily combined with Eq. (2.10) to reach several important conclusions on the dislocation structure and dynamics. The surface current entering Eq. (2.10) is, by Eq. (2.11) of Chapter 2,

$$-J_1(M_1(x_c), M_0) = T_{11} M_1(x_c) + u_{11} M_1^3(x_c) \quad (2.16)$$

with,

$$T_{11} = -r_1 + u_{12} M_0^2 = -r_1 + u_{12} r_2 / u_{22}. \quad (2.17)$$

Here, T_{11} is positive within the stability range of the rippled phase R_2 [see the Appendix A of Chapter 2] and vanishes at the R_2 -to- RhP transition. Away from the transition ($T_{11} \neq 0$), it is possible to ignore the $[M_1(0)]^3$ term in Eq. (2.16) [as justified in the following]. So, for $T_{11} \neq 0$

$$-J_1(M_1(x_c), M_0) \sim M_1(x_c),$$

and thus, by Eqs. (2.10) and (2.12),

$$v \lambda \sim \frac{M_1(x_c)}{M_0} = \frac{\lambda}{\xi_c}. \quad (2.18)$$

Thus, the dislocation velocity $v \sim 1/\xi_c$. This fact is easily combined with the scaling relation Eq. (2.15b) to reach the following conclusions: For $T_{11} \neq 0$ dislocation velocity scales as

$$v \sim \frac{1}{\xi_c} \sim \frac{1}{\lambda^{3/2}}, \quad (2.19a)$$

whereas dislocation aspect ratio scales as,

$$\frac{M_1(x_c)}{M_0} \sim \frac{\lambda}{\xi_c} \sim \lambda v \sim \frac{1}{\lambda^{1/2}}. \quad (2.19b)$$

Eq. (2.19a) will be used in Sec. III of this chapter to discuss the coarsening dynamics of the rippled states on (110) surfaces. Eq. (2.19b) exemplifies the anticipated before fact that, as

$$\xi_c \sim \lambda^{3/2}, \quad (2.19c)$$

the dislocation aspect ratio λ/ξ_c becomes small, i.e., that dislocations become very sharp in the important limit of large λ that is reached at long times. In this limit, $M_1(x_c)$ approaches zero [see Eq. (2.19b)]. Due to this fact, in the above discussion it was appropriate to ignore the cubic term in Eq. (2.16), for $T_{11} \neq 0$.

On the other hand, at the R_2 -to- RhP transition ($T_{11} = 0$), by Eq. (2.16), $-J_1(M_1(x_c), M_0) \sim (M_1(x_c))^3$, and thus, by Eq. (2.10),

$$v\lambda \sim (M_1(x_c))^3 \sim (\lambda/\xi_c)^3. \quad (2.20)$$

Combining the scaling relations in Eqs. (2.20) and (2.15b) yields

$$v \sim \frac{1}{\lambda^{7/4}} \quad (2.21a)$$

and

$$\frac{M_1(x_c)}{M_0} \sim \frac{\lambda}{\xi_c} \sim \frac{1}{\lambda^{1/4}}, \quad (2.21b)$$

at the rippled-to- RhP state transition. By comparing the two different velocity laws in Eqs. (2.21a) and (2.19a), we see that, for a given λ , the dislocations are typically slower

at the transitions. This yields slower coarsening at the transition, with a distinct coarsening exponent discussed in Sec. III of this chapter. This phenomenon has been evidenced also in our simulations, see Sec. IV of Chapter 2 and the Fig. 7(a) therein. It shows through a significant depression of the interface roughness that occurs on the R_2 -to- RhP transition at $a = a_-$.

Away but close to this transition, there is a crossover behavior, which is significant for small nonzero values of $T_{11} \sim a_- - a > 0$. In our simulations, this crossover manifests itself through the depression of the interface width, not only at the R_2 -to- RhP transition but also away from it, see Fig. 7(a) of Chapter 2. To analyze this crossover phenomenon quantitatively, we re-express the dislocation dynamics law in Eq. (2.14) by changing the integration over x_1 into integration over M_1 . It can be done using Eq. (2.8) that implies

$$vM_1 = \frac{\partial J_1(M_1, M_0)}{\partial M_1} \frac{dM_1}{dx_1}. \quad (2.22)$$

Thus,

$$dx_1 = \frac{1}{vM_1} \frac{\partial J_1(M_1, M_0)}{\partial M_1} dM_1 \quad (2.23)$$

By Eq. (2.23), our Eq. (2.14) can be transformed into

$$\frac{\sigma}{\lambda} = - \int_0^{M_1(x_c)} dM_1 M_1 \frac{\partial J_1(M_1, M_0)}{\partial M_1} \quad (2.24)$$

For a given form of $J_1(M_1, M_0)$, the integral in Eq. (2.24) can be explicitly calculated.

Thus, by Eq. (2.16),

$$\frac{\sigma}{\lambda} = \frac{1}{2} T_{11} (M_1(x_c))^2 + \frac{3}{4} u_{11} (M_1(x_c))^4. \quad (2.25)$$

Eq. (2.25) enables to calculate $M_1(x_c)$ directly, for a given λ . In addition, by Eqs. (2.10) and (2.16), we also have

$$M_0 v \lambda = T_{11} M_1(x_c) + u_{11} (M_1(x_c))^3 \quad (2.26)$$

The biquadratic equation (2.25) can be analytically solved for $M_1(x_c)$, and, furthermore, this solution can be inserted into Eq. (2.26). Eventually, this yields a closed expression for the dislocation velocity as a function of λ . There is no need for us to exhibit here this lengthy formula, since the basic features significant for the aforementioned crossover are clear already from the structure of Eqs. (2.25) and (2.26). From both of them we see that the crossover occurs when $T_{11} \approx u_{11} (M_1(x_c))^2$, i.e., for

$$M_1(x_c) \approx M_{cross} = (T_{11}/u_{11})^{1/2}. \quad (2.27)$$

By Eq. (2.25), this corresponds to the crossover value of λ of the form

$$\lambda_{cross} \approx \frac{\sigma}{T_{11} (M_{cross})^2} \approx \frac{\sigma}{u_{11} (M_{cross})^4} \sim \frac{1}{(T_{11})^2} \sim \frac{1}{(a_- - a)^2} \quad (2.28)$$

Next, by Eqs. (2.25) and (2.26), for $\lambda < \lambda_{cross}$, i.e., $M_1(x_c) > M_{cross}$,

$$v(\lambda) \cong \left(\frac{4}{3}\right)^{3/4} \frac{u_{11}^{1/4} \sigma^{3/4}}{\lambda^{7/4}} \sim \frac{1}{\lambda^{7/4}}. \quad (2.29)$$

Thus, for $\lambda < \lambda_{cross}$ one has the scaling behavior seen at the *R*-to-*RhP* transition, Eq.

(2.21a). On the other hand, for $\lambda > \lambda_{cross}$, i.e., $M_1(x_c) < M_{cross}$, by Eqs. (2.25) and (2.26),

$$v(\lambda) \cong \frac{(2\sigma T_{11})^{1/2}}{M_0 \lambda^{3/2}} \sim \frac{(a_- - a)^{1/2}}{\lambda^{3/2}}, \quad (2.30)$$

Thus, for $\lambda > \lambda_{cross}$ one has the ultimate scaling behavior seen off the transition critical point, Eq. (2.19a). As this transition point is approached, λ_{cross} diverges, and one is left

with the purely critical scaling behavior in Eq. (2.29), i.e., Eq. (2.21). In the following section, we discuss the effects of this significant crossover on the interfacial coarsening dynamics.

III. COARSENING DYNAMICS OF RIPPLED STATES ON (110) SURFACES

As evidenced by our simulations in Sec. IV of Chapter 2, the coarsening growth of rippled state period λ is mediated by traveling dislocations, in a way similar to the one discussed by Moldovan and Golubovic (Ref. [19] of Ch. 1, denoted as MG in the following) before, for the pyramidal phases on (100) surfaces. In fact, these surfaces coarsen by the motion and annihilation of two nearly independent ensembles, moving along the two principal axes of the (100). Geometrically, each of these ensembles is equivalent to the rippled state dislocation ensemble. Due to this, a few of the basic (geometric in origin) relations for the growth of λ can be adopted here from MG. These are: (i) the relation

$$\frac{1}{\lambda} \frac{d\lambda}{dt} = \frac{2v(\lambda)}{\xi(\lambda)}, \quad (3.1)$$

with, ξ , the separation between dislocations along a ripple, and (ii) the relation

$$\xi \sim \lambda^{q-1}, \quad (3.2)$$

with $q = 3$, the number of channels for dislocation annihilations. The crucial difference between the dislocations of the four-sided pyramidal phases on (100) surfaces, discussed in MG, and those of the rippled states discussed by us in Sec. II of this Chapter, is in their velocity law $v(\lambda)$. This difference affects the detailed form of the coarsening law giving the growth of $\lambda(t)$ vs. time. By Eqs. (3.1) and (3.2), this growth law can be extracted from

$$t = \int_0^{\lambda(t)} \frac{d\lambda}{\lambda} \frac{\xi(\lambda)}{v(\lambda)} \sim \int_0^{\lambda(t)} \frac{d\lambda}{\lambda} \frac{\lambda^{q-1}}{v(\lambda)}. \quad (3.3)$$

Eq. (3.3) can be combined with the dislocation velocity laws, $v(\lambda)$ we derived in Sec. II of this Chapter, to obtain the coarsening laws governing the dynamics of rippled states on (110) surfaces. For this purpose, we note that for the velocity laws of the form

$$v(\lambda) \sim \frac{1}{\lambda^{n_v}}, \quad (3.4)$$

the equation (3.3) is easily shown to imply the coarsening laws,

$$\lambda(t) \sim t^{n_\lambda}, \quad \xi(t) \sim t^{n_\xi}, \quad (3.5)$$

with,

$$n_\lambda = \frac{1}{q-1+n_v}, \quad (3.6)$$

and,

$$n_\xi = (q-1)n_\lambda = \frac{q-1}{q-1+n_v}. \quad (3.7)$$

In the presence of the crossover discussed at the end of Sec. II of this Chapter, $v(\lambda)$ is not of a simple power law form as in Eq. (3.4). Thus, Eq. (3.3) needs to be combined with the results of Sec. II to derive the actual growth law of $\lambda(t)$. Nonetheless, since $v(\lambda)$ has power law asymptotic forms on both sides of the crossover, the crossover behavior of $v(\lambda)$ versus λ simply implies a crossover behavior of $\lambda(t)$ and $\xi(t) \sim [\lambda(t)]^{q-1}$ versus time. The crossover time can be easily obtained by combining Eq. (3.3) with Eqs. (2.28) and (2.29). Thus, we reveal the crossover time scale,

$$t_{cross} \sim \frac{1}{T_{11}^{2q+3/2}} = \frac{1}{T_{11}^{15/2}}, \quad (3.8)$$

which is diverges at the ripple-to-*RhP* state transition, because $T_{11} \sim a_- - a$ vanishes at this transition. For $t < t_{cross}$, one has $\lambda < \lambda_{cross}$, and $v(\lambda)$ is as in Eq. (2.21a) [i.e., Eq. (2.29)], corresponding to Eq. (3.6) with the velocity exponent $n_v = 7/4$. With this value of n_v , by Eqs. (3.6) and (3.7), with $q=3$ [see MG], we find that $w(t) \sim \lambda(t) \sim t^{n_\lambda}$ and $\xi \sim t^{n_\xi}$, with

$$n_\lambda = \frac{4}{15} \cong 0.2666, \quad n_\xi = \frac{8}{15} \quad (3.9)$$

At the ripple-to-*RhP* transition, the crossover time $t_{cross} \rightarrow \infty$, and the coarsening with the exponents in Eq. (3.9) should persist at arbitrarily long times. We checked this result by doing simulations at the transition point at $a = a_-$. Off this transition, in the rippled phase, t_{cross} is finite, and for $t > t_{cross}$, one has $\lambda(t) > \lambda_{cross}$, and $v(\lambda)$ is as in Eq. (2.19a) [i.e., Eq. (2.30)] corresponding to the velocity exponent $n_v = 3/2$. With this value of n_v , by Eqs. (3.6) and (3.7), with $q = 3$ [see MG], we find $w \sim \lambda \sim t^{n_\lambda}$ and $\xi \sim t^{n_\xi}$, with

$$n_\lambda = \frac{2}{7} \cong 0.2857, \quad n_\xi = \frac{4}{7} \quad (3.10)$$

In fact, by Eqs. (2.30) and (3.3), we find, for $t > t_{cross}$,

$$w(t) \sim \lambda(t) \sim (a_- - a)^{1/7} t^{2/7}, \quad (3.11)$$

indicating that the amplitude of this coarsening law vanishes at the R_2 -to-*RhP* transition. At the transition, the coarsening in Eq. (3.11) is pushed away to infinite times and replaced by Eq. (3.9), with the coarsening law $w(t) \sim \lambda(t) \sim t^{4/15}$. Away from the transition point, this critical coarsening behavior eventually crosses over to the coarsening law in Eq. (3.11), with a bigger coarsening exponent $n_\lambda = 2/7 \cong 0.2857$. This

coarsening exponent is in a very good agreement with the values obtained from simulations of the rippled states, discussed in Sec. IV of Ch. 2, away from the critical point. Also, the simulations in Fig. 7(a) of Ch. 2 indicate that the amplitude of the coarsening law decreases as the R_2 -to- RhP transition approached. This is in accord with the depression of this amplitude suggested by Eq. (3.11) of this chapter.

To summarize, the above analytic results explain the coarsening with

$$\lambda \sim t^{2/7}, \quad \xi \sim t^{4/7} \quad (3.12)$$

seen in our simulations of the rippled phase, see Fig. 9(b) of Ch. 2 and discussion therein.

We recall however that, under some circumstances, a different coarsening, with,

$$\lambda \sim t^{1/3}, \quad \xi \sim t^{1/2} \quad (3.13)$$

is also seen in the rippled state, see Fig. 9(c) of Ch. 2 and discussion therein. In the phase diagram, such a coarsening occurs only in a subdomain of the rippled state, which exist if the parameter $c \neq 0$. For this case, the effective free energy, invoking in deriving the coarsening in Eq. (3.12), does not exist [see Eq. (2.14) here and our discussions in Ch. 2]. This feature is responsible for the existence of the Buckled Rippled state, and, apparently, also for the existence of the rippled state subdomain with the coarsening in Eq. (3.13). Morphology of the dislocations in this subdomain, as obtained from our simulations, is shown in Fig. 8(b) of Ch. 2. Typical for these knife dislocations are long cores with the core size ξ_c comparable to the separation between dislocations ξ ,

$$\xi \sim \xi_c. \quad (3.14)$$

By invoking here Eq. (2.19c) of this chapter, we find

$$\xi \sim \lambda^{3/2}. \quad (3.15)$$

Equation (3.15) is of the form of the equation (3.2), with $q = 5/2$. With this value of q , and $n_v = 3/2$ as before, the equations (3.6) and (3.7) yield

$$n_v = \frac{1}{3}, \quad n_\xi = \frac{1}{2}. \quad (3.16)$$

These exponents are indeed in accord with the scaling behavior in Eq. (3.13) suggested by our simulations in Fig. 9(c) of Ch. 2.

Next, we discuss the coarsening behavior of Rectangular Rippled states. Our simulations in Sec. IV of Chapter 2 suggest that for these phases,

$$\lambda \sim t^{1/4}, \quad \xi \sim t^{1/2}. \quad (3.17)$$

The scaling behavior in Eq. (3.17) can be also understood within the analytic framework of this chapter. To see this, we note that the dislocations of the Rectangular Rippled States are qualitatively different from the dislocations of ordinary rippled states [hence, the scaling behavior in Eq. (3.17) is different from that we find for simple rippled states in Eqs. (3.12) and (3.13)]. Indeed, consider a typical dislocation of the Rectangular Rippled state, depicted in Fig 2 for the case of the $R_2^{(rec)}$ state. The core of this dislocation is a R_1 facet having the shape of rhomb, see Fig. 2(b). The rhomboidal angle ψ in Fig. 2(b) is fixed by model parameters, i.e., it does not depend on the dislocation size. Due to this geometric constant, the lateral core size ξ_c is simply proportional to λ ,

$$\xi_c \sim \lambda. \quad (3.18)$$

By Eqs. (3.18) and (2.15b), we find the velocity law for the dislocations in Rectangular Rippled states, in the form,

$$v \sim \frac{1}{\lambda^2}. \quad (3.19)$$

FIG. 2. Interface profile [Fig. (a)] and the corresponding facet edges [Fig. (b)] in the vicinity of a dislocation of the Rectangular Rippled state $R_2^{(rec)}$. The dislocation moves to the right in Fig. (b). The dislocation core as actually an R_1 facet. This facet is a rhomb with the rhomboidal angle ψ , i.e., the dislocation aspect ratio, which does not depend on the dislocation size. Due to this, the lateral core size ξ_c is simply proportional to λ .

This dislocation velocity law corresponds to Eq. (3.4) with the velocity exponent $n_v = 2$.

With this value of n_v , by Eqs. (3.6) and (3.7), with $q = 3$ [see MG], we find

$$n_v = \frac{1}{4}, \quad n_\xi = \frac{1}{2}. \quad (3.20)$$

These exponents are indeed in accord with the scaling behavior in Eq. (3.17) that has been suggested by our simulations of the Rectangular Rippled states.

Chapter 4

EPITAXIAL GROWTH AND EROSION ON (001) CRYSTAL SURFACES: FAR-FROM-EQUILIBRIUM TRANSITIONS, INTERMEDIARY STATES, AND VERTICAL ASYMMETRY

I. INTRODUCTION

Growing surface nano-structures induced by the Ehrlich-Schwoebel-Villain instability [1], are often observed in molecular-beam epitaxy growth and erosion on various crystal surfaces. This is documented by numerous experiments and simulations on (001), (111), and (110) crystal surfaces, [2-14]. On square symmetry surfaces, nearly periodic (defected) checker-board arrangements of alternating four-sided pyramids and pits (inverted pyramids) frequently develop, with sizes growing in time as $t^{1/4}$, as

exemplified by the Cu(001) growth [2]. This coarsening law has been understood only recently, in terms of the dynamics of topological defects (dislocations) of the regular checkerboard structure, as elucidated by Moldovan and Golubovic [3] and by Siegert [4]. However, other structures have been recently inferred on (001) surfaces, [10-14]. Moreover, a far-from-equilibrium phase transition between two kinds of pyramidal states has been very recently seen in the growth on Ag(001), by de Mongeot *et al.* [10]. They report a 45-degree rotation of pyramid facets at a low $T \approx 100$ K, and attribute it to deactivation of corner crossing processes, [5]. Coincidentally, at significantly higher temperatures, in erosion on Cu(001), a similar transition has been seen by Broekmann *et al.*, and, at the same time, disputed [11].

There is a lack of deep qualitative understanding of these recent findings, whereas some long-standing basic questions remain unresolved, even for the common (001) surfaces. How does the well-known vertical (pyramid-pit) asymmetry affect interface coarsening dynamics? What is the real nature of the recently revealed multitude of interfacial morphologies possible to occur on (001), and what is the real nature of the surface nanostructures involved in the recently revealed far-from equilibrium transitions seen on (001)? Here, we answer these questions, both recent and long-standing.

In this Chapter, by taking into account the square symmetry of (001) surface, we construct interface dynamical model, which is the first one to exhibit the *generic* multitude of interfacial states and transitions in the epitaxial growth and erosion on *any* (001) crystal surface. We use our model to discuss the 45-degree pyramid facet rotation transition on realistic (001) crystal surfaces. We reveal that this transition is, necessarily, a sequence of two transitions. Between these transitions our model shows that a few

interesting intermediary states of interface develop. We show that the presence of these intermediary states causes an enhanced interface roughening that were seen by Stoldt *et al* [12] in the experiment of MBE growth on the Ag(100) crystal surface. In addition, we predict the form of surface diffraction data for our new intermediary states. Our theoretical predictions for SD (out-of-phase diffraction pattern) and FT (in-phase diffraction pattern) can be used to distinguish these two intermediary states in future experiments and numerical studies. And for the first time, we have elucidated the actual effects of the elusive vertical growth asymmetry on the multitude of states on (001) crystal surfaces.

II. SYMMETRIES OF (100) SURFACES AND INTERFACE DYNAMICS

We will elucidate the epitaxial growth and erosion on (001) crystal surfaces by considering the general phenomenological model [1, 6] for the epitaxial growth and erosion in the absence of the creation of surface vacancies. It expresses the dynamics of the interface profile $h(x_1, x_2, t)$ in the form of the conservation law involving the surface current $\vec{J} = (J_1, J_2)$

$$\frac{\partial h}{\partial t} = -\vec{\nabla} \vec{J}, \quad \vec{J} = \vec{J}^{NE}(\vec{M}) + \vec{J}^{curv}. \quad (2.1)$$

Here, as in Ch. 2, $\vec{J}^{NE}$ the surface non-equilibrium current being a function of the local interface slope vector $\vec{M} = (M_1, M_2) = \vec{\nabla} h$. In Eq. (2.1), $\vec{J}^{curv}$ includes other, curvature currents that vanish on flat interfaces (facets), such as the usual surface diffusion Mullins current $\sim \vec{\nabla}(\vec{\nabla})^2 h$, and the *Vertical Asymmetry* (VA) Villain current

$$\vec{J}_{VA} = -\frac{\lambda}{2} \vec{\nabla}(\vec{\nabla} h)^2 \quad (2.2)$$

breaking the vertical reflection symmetry $h \rightarrow -h$, [1,6].

The (001) surface has square symmetry imposing a few ubiquitous properties of $\vec{J}^{NE}(\vec{M}) = (J_1^{NE}(\vec{M}), J_2^{NE}(\vec{M}))$. It must transform in the same way the slope vector $\vec{M}$ transforms under symmetry transformations of (001). Thus, under the simple square reflections:

$$\begin{aligned} (M_1, M_2) &\rightarrow (-M_1, M_2) \\ (J_1^{NE}, J_2^{NE}) &\rightarrow (-J_1^{NE}, J_2^{NE}) \end{aligned} \quad (2.3)$$

and

$$\begin{aligned}(M_1, M_2) &\rightarrow (M_1, -M_2) \\ (J_1^{NE}, J_2^{NE}) &\rightarrow (J_1^{NE}, -J_2^{NE}) .\end{aligned}\tag{2.4}$$

Also, square diagonal reflection symmetry implies

$$\begin{aligned}(M_1, M_2) &\rightarrow (M_2, M_1) \\ J_1^{NE}(M_1, M_2) &\rightarrow J_2^{NE}(M_2, M_1) .\end{aligned}\tag{2.5}$$

III. KINETIC PHASE DIAGRAM FOR (001) SURFACE

In this section, we will discuss the form of the surface non-equilibrium current $\vec{J}^{NE}(\vec{M})$ for (001) surfaces and develop kinetic phase diagram for these surfaces. Commonly, solutions (zeros) of $\vec{J}^{NE}(\vec{M}) = \vec{0}$ are related to the preferred slopes $\vec{M}$ of the facets that develop across the growing interface and organize themselves into pyramidal structures, [3,4]. By the square symmetry of (001), there are *three* possible kinds of these preferred slope vectors $\vec{M} = (|\vec{M}|\cos\theta, |\vec{M}|\sin\theta)$:

(i) *Singlet*, at $|\vec{M}| = 0$ [Fig. 1(a)];

(ii) *Quartet* of four equivalent (symmetry related) slope vectors [Fig. 1(b)]. There are two *non-equivalent* types of quartets: Type I quartet, along square diagonals, $\theta = 45^\circ + 90^\circ(n-1)$, $n = 1, 2, 3, 4$, and Type II quartet, along square sides, $\theta = 90^\circ(n-1)$, $n = 1, 2, 3, 4$. Importantly for the following, the two quartets are *not* equivalent to each other because the 45-degree rotation is not a symmetry of (001);

(iii) *Octet* of eight equivalent slope vectors pointing along the *eight* polar angles: $\theta = 90^\circ(n-1) \pm \phi$, where ϕ is an angle in the range $-45^\circ < \phi < +45^\circ$, and $n = 1, 2, 3, 4$, see Fig. 1(c).

In the unstable epitaxial growth, the singlet at $\vec{M} = \vec{0}$ is unstable, and preferred facets may thus correspond to the quartets or to an octet. Thus, stable Type I quartet may give rise to the checkerboard Phase I (*P I*) pyramidal structure, see Fig. 2. Likewise, stable Type II quartet may give rise to the checkerboard Phase II (*P II*) pyramidal

FIG. 1. Types of zeros of the surface nonequilibrium current on (001): (a) singlet, (b) two types of quartets, (c) octet.

structure in Fig. 2. The states P I and P II *both* enter the figure 2, giving our unified far-from-equilibrium phase diagram for the epitaxial growth and erosion phenomena on (001) surfaces, derived in the following. Type I and Type II facets are geometrically related by the 45-degree rotation. Our diagram thus reproduces the recently observed 45-degree facet rotation transition on Ag(001) seen by de Mongeot *et al.*, [10]. Moreover, we find that the uncommon Octet zeros give rise to a novel interface state, seen in Fig. 2 (a) from our simulations. There, it intervenes between P I and P II, and its signature is the interface slope distribution (SD) function in Fig 2(a), with eight peaks forming an octagon in the $\vec{M}$ plane, at the eight polar vectors $\theta = 90^\circ (n-1) \pm \phi$, $n = 1, 2, 3, 4$. Thus, we call it the *Octagonal Pyramid (OctP)* state. From simulations, we find that *OctP* corresponds to a structure with pyramids having *up to* eight facets, see Fig. 3(a). Notably, the SD of our *OctP*, with eight peaks positioned as in Fig. 2(a), is the same as the SD of the intermediary state revealed by Broekmann *et al.*, [11] in the 45-degree rotation transition on Cu(001); see the eight lobe out-of-phase diffraction patterns in Ref. [11]. It has been however suggested that the 45-degree rotation transition on Cu(001) (erosion) is an effect of post-erosion annealing, [11]. On the other hand, for the Ag(001) growth, such post-growth annealing effects are carefully eliminated at the low $T \approx 100$ K where the transition occurs, [10]. It can be thus addressed as a far-from-equilibrium growth transition.

We proceed to expose general phenomenology of the epitaxial growth and erosion on common (001) surfaces, by considering the kinetic model Eq. (2.1) with generic form of the non-equilibrium current $\vec{J}^{NE}(\vec{M})$. It can be obtained as an expansion in powers of $\vec{M}$ respecting the stringent restrictions imposed by the square symmetry of (001). By the

FIG. 2. The kinetic phase diagram of the interface model with $\tilde{J}^{NE}(\vec{M})$ in Eq. (3.1). We depict it in the $(b, W = wu^2/r)$ plane for fixed c and d . The point I is at $b=1, W=0$. In (a): the case $(d-1)(c-d-1) < 0$, with *OctP* realized. In (b): the case $(d-1)(c-d-1) > 0$, with *MultiP* realized. We give interface height contour plots, height FTs (yielding in-phase diffraction patterns), and SD functions (yielding out-of-phase diffraction patterns), from our simulations. The *OctP* angle ϕ in (a) changes from 0 (at the transition to *P II*) to 45° (at the transition to *P I*). For all data here, $VA = 0$.

a)

b)

FIG. 3(a,b). *OctP* state: interface height contour plots [left panel] and facet edges plots [right panel](contour plots of the interface curvature magnitude). Note sharp (dark) edges at pyramid bases, and blunt (faint) edges emerging from pyramid tops. (b) *MultiP* state pyramids, formed out of both Type I and Type II facets: Note that the spatial arrangement of *MultiP* pyramids is as in Phase I [see also Figs. 2(b) and 4(b) right panel]. For all data here, $VA = 0$.

FIG. 3(c). Square of interface width, $\langle h^2 \rangle$ versus b for a fixed W for several times, increasing from bottom to top: Note the enhanced roughening in the proximity of the intermediary state [here, *MultiP*] between the dashed lines.

inversion symmetry of (001), this expansion must contain only odd powers of $\vec{M}$. By respecting the square reflection symmetries, we arrive at the general expansion of the form,

$$\begin{aligned} J_1^{NE} &= M_1[r - u(M_1^2 + bM_2^2) - w(M_1^4 + cM_1^2M_2^2 + dM_2^4) + \dots], \\ J_2^{NE} &= M_2[r - u(M_2^2 + bM_1^2) - w(M_2^4 + cM_2^2M_1^2 + dM_1^4) + \dots]. \end{aligned} \quad (3.1)$$

The ubiquitous 5th order in M , w -terms in Eq. (3.1) are essential for the correct qualitative understanding the 45-degree transition on realistic (001) surfaces. In fact, for $w \sim W = 0$, the 45° rotation transition occurs at a single point I at $(b = 1, W = 0)$ in Fig.

2. There, $\vec{J}^{NE}(\vec{M}) = \vec{0}$ vanishes on a circle $|\vec{M}|^2 = r/u$. However this vanishing of crystal anisotropy is unphysical and *in general* excluded on (001). Thus, the ubiquitous w -terms in Eq. (3.1), breaking this artificial symmetry, *must* be included to discuss the transition. The w -terms are directly responsible for our novel, ubiquitously present intermediary states *OctP* and *MultiP* (see below) seen for $w \neq 0$ in the kinetic phase diagram in Fig. 2.

For typical situations with small selected $|\vec{M}|$, the minimal, basic growth model for (001) is actually obtained by truncating out the higher order terms in the ellipses in Eq. (3.1). In this limit, we model $\vec{J}^{curv}$ as described below Eq. (2.1). In particular, through the Villain current in Eq. (2.2), we include the effects of the vertical asymmetry (VA). Such a minimal model exhibits a number of interfacial states generic for (001) crystal surfaces, seen in the (far-from-equilibrium) phase diagram, Fig. 2. Like in Ch. 2, our kinetic phase diagram is deduced by linear stability analysis of the facets corresponding to the zeros of $\vec{J}^{NE}(\vec{M})$ in Eq. (3.1), and further corroborated by numerical simulations of the model in Eqs. (2.1), and (3.1). The model yields the 45°

rotation transition between P I and P II in Fig. 2. There we see also our aforementioned intermediary $OctP$ state, which occupies in Fig. 2(a) a region in which neither Type I nor Type II facets are stable. Interestingly, though many sided, $OctP$ pyramids have the same coordination (spatial arrangement), and thus yield qualitatively the same Fourier transforms (FT), i.e., in-phase-diffraction pattern, as the four sided pyramids of a nearby checkerboard state, see Fig. 2(a).

There is one more, qualitatively different intermediary state called as $MultiP$ in Fig. 2(b): There, the 45° rotation transition goes through a *multi-stable* region in which Type I and Type II quartet facets [Fig. 1(b)] are *both* stable. In this region, SD (thus, also the out-of-phase-diffraction) also has eight peaks [see Fig. 2(b)]. However, in contrast to the SD of $OctP$ in Fig. 2(a), the eight SD peaks of the $MultiP$ in Fig. 2(b) are not equivalent to each other: Note that SD of $MultiP$ structures as a superposition of the nearby P I and P II SD peak patterns, with strong sharp peaks along Type II facets directions, and broad weaker peaks along Type I facets directions. Corresponding to this are multisided pyramids (with *up to* eight sides) with prominent Type II facets (like in the P II state) see Figs. 2(b), 3(b), and 4(b). However, this state has spatial arrangement of pyramids which is the same as that of the P I state [see interface plots and their FTs in Figs. 2(b), 3(b) and 4]. Thus, the $MultiP$ is a *hybrid* state - it is neither P I nor P II state. For $VA = 0$, $MultiP$ has the pyramid spatial arrangement of P I *already* at early times. For $VA \neq 0$, $MultiP$ pyramids initially form with the spatial arrangement of P II, see Fig. 4(b) left panel. Eventually, however, the pyramid lattice rearranges, and spatial arrangement becomes the same as that of P I, see Fig. 4(b) right panel. This striking spatial rearrangement of $MultiP$ is documented also by the time sequence of FTs in Fig.

FIG. 4(a). VA effects on the *MultiP* intermediary state. Interface width $\langle h^2 \rangle^{1/2} \sim t^{1/3}$, both with and without VA .

b)

c)

FIG. 4(b,c). VA effects on the *MultiP* intermediary state. (b) Due to $VA \neq 0$, at early times (left panel) the pyramids form with the spatial arrangement of the Phase II. However, at later times (the right panel), the spatial pyramid arrangement turns into that of the Phase I. This spatial rearrangement is illustrated also by the time sequence of FTs in (c), at $t_1 < t_2 < t_3$.

4(c). Interestingly, we do not find such dramatic transient VA effects on the other, *OctP* state.

We find from our simulations that the pyramid sizes in *MultiP* and *OctP* states grow as $t^{1/3}$, both with and without VA, see Fig. 4(a). We find that both intermediary states coarsen via local pyramid (or pit) coalescence. For $(b = 1, W = 0)$, at the isotropic transition point *I* in Fig. 2, pyramids form with randomly oriented facets and grow as $t^{1/3}$ via local pyramid coalescence, [3]. However for realistic (001) surfaces $w \sim W \neq 0$, and the transition ubiquitously goes through our intermediary states in Fig. 2. In this states, the pyramid facets are oriented by (001) anisotropy. However, they still grow as $t^{1/3}$ via local coalescence, as revealed by our simulations here. These numerical results evidence striking robustness of the $t^{1/3}$ law for the growth via local pyramid coalescence.

Away from the intermediary states in Fig. 1, pyramid sizes in checkerboard states *P I* and *P II* grow as $t^{1/4}$, both with and without VA, see Fig. 5(a). This growth proceeds via topological defects (dislocations) of the checkerboard [3], see Figs. 5(b) and (c): Note that VA introduces two kinds of pyramid facet edges, sharp and blunt. However, this decoration of the edges mash does not affect the topology of the *defected* checkerboard. In accord with experiments [2], these results for the first time explain the striking insensitivity of the (zero VA) checkerboard $t^{1/4}$ growth law [3], to the presence of VA. Both with and without VA, in the *proximity* of the intermediary states, the coarsening mechanism changes into coalescence yielding the *enhanced roughening* manifested through the $t^{1/3}$ growth at long times and, also, a faster growth at short times *as well*, see Fig. 3(c). It is enlightening to elucidate various recent experiments on Ag(001) growth by

FIG. 5(a). VA effects on checkerboard structure (away from intermediary states regions). Interface width for three different strengths of VA (increasing from zero, from bottom to top): $\langle h^2 \rangle^{1/2} \sim t^{1/4}$ both with and without VA.

b)

$$VA = 0$$

c)

$$VA \neq 0$$

FIG. 5(b,c). VA effects on checkerboard structure (away from intermediary states regions). Surface without [in (b)] and with VA [in (c)]. In (c), note blunt (faint) facet edges emerging from pyramid tops, and sharp (dark) edges emerging from the pits.

using these findings of our theory. Indeed, our enhanced roughening has been seen by Stoldt *et al.* [12] in the proximity of the temperature ≈ 100 K, *exactly* where de Mongeot *et al.* [10] report the 45° rotation transition. Thus, within a unified framework, our theory ties together previously disconnected findings on Ag(001) growth. By the above discussions, we predict that either *MultiP* or *OctP* state develops on Ag(001) and intervenes in the 45° rotation transition. We note that, in contrast to our model, the previous KMC models of Ag(001) in Refs. [12-14] (by construction) do not exhibit the facet rotation transition seen in the experiments, Ref. [10].

In summary, by a consistent physical account of the square symmetry, our model is the first one to exhibit the *generic* multitude of interfacial states and transitions in the epitaxial growth and erosion on *any* (001) crystal surface. We have revealed for the first time that the 45° rotation phenomenon on realistic (001) surfaces is ubiquitously a sequence of two transitions. Between them, our intermediary states ubiquitously develop and cause an enhanced interface roughening. Our results for out-of-phase (SD) and in-phase (FT) diffraction patterns can be used to distinguish our intermediary states in future experiments and numerical studies. And for the first time, we have elucidated the actual effects of the elusive vertical growth asymmetry on the multitude of states on (001) crystal surfaces.

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