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The Influence of Edge Energy on Step Flow Instability for Crystals with Bravais Versus Non-Bravais Lattice Structures

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Abstract. We examine the meandering instability for prismatic lattices formed from triangles, squares and hexagons using a nearest neighbor kinetic Monte Carlo model. In the first two cases, which are Bravais lattices, we find that facets with the orientation favored in the equilibrium shape of isolated islands are most prone to this instability, while the analogous facet for the hexagonal lattice is the least unstable. We argue that this is due to a significant difference in the reconstructed/equilibrium versus the non-reconstructed edge energy for non-Bravais crystals. Surface/edge energy is typically modeled as a single-valued function of orientation. We put forward a simple geometric argument that suggests this picture is inadequate for crystals with a non-Bravais lattice structure. In the case of a hexagonally structured lattice, our arguments indicate that the non-reconstructed edge energy can be viewed as both discontinuous and multi-valued for a subset of orientations that are commensurate with the crystal structure. We support these conclusions with density functional theory calculations that also reveal multivalued surface energies for the set of singular orientations.

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1 Introduction

In this paper we use kinetic Monte Carlo (KMC) simulations and their underlying lattice models to explore the way surface energy behaves for Bravais versus non-Bravais

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crystals. The effect we identify would appear to be generic to non-Bravais systems, but we illustrate it in detail for a nearest-neighbor model with hexagonally structured layers. Our reason for examining this particular case is that it is the hexagonal analog of the ubiquitous solid-on-solid or, more descriptively, cube-on-cube model that has been used to understand many fundamental aspects of epitaxial growth.

In continuum models the term surface energy normally refers to the surface free energy γ_f, so that it includes entropic effects within some thermodynamic ensemble. This is modeled as a continuous function of surface/edge orientation, $\gamma_f(\hat{\mathbf{n}})$ [1,2], and this function is often constructed so that it is consistent with underlying symmetry constraints combined with experimental observations or data from computations [3,4]. In contrast, the surface energies γ derived from bond counting models are zero-temperature surface energies — entropic effects are introduced via the rates in the KMC model. Most surface energies computed with density functional theory (DFT) are also zero-temperature results.

Often there is a further distinction between equilibrium/reconstructed and non-reconstructed surface energies of ideally truncated planar surfaces. In a lattice based bond-counting model, one can define an unreconstructed surface energy $\bar{\gamma}(\mathbf{n})$ as the number density of broken bonds formed by cutting along a perfectly flat plane or line. In a DFT calculation, one can define a similar quantity where, after the cut is made, the surface is allowed to relax by strict energy descent to a local minimum. This is often a meta-stable configuration. Alternatively, one can define a reconstructed surface energy $\tilde{\gamma}(\mathbf{n})$ by allowing the atoms to reconfigure after the cleaving surface/edge is introduced, so that a global minimum is obtained. For the bond-counting models, one would do this subject to the lattice constraint, whereas the DFT calculations would be constrained by periodic boundary conditions. While the non-reconstructed surface energies defined using metastable states may play no role in the equilibrium behavior of the system, the KMC simulations presented below suggest they are important for the dynamics of some non-equilibrium processes. We find that the non-reconstructed surface energy of non-Bravais crystals is both multivalued and discontinuous. This is due to the fact that some orientations give rise to a translation invariant pattern of broken bonds, while others do not.

After deriving the surface energies, as defined above, for the triangular, cubic and hexagonal lattices, we will present a few DFT calculations that support our conclusions before moving on to exploring step-flow dynamics during the epitaxial growth of many layers of each crystal structure. The KMC simulations reveal that something close to the equilibrium/reconstructed behavior is rapidly achieved in many scenarios. For example, if we consider the surface energy of uniformly propagating steps at various crystal orientations, we find near-equilibrium behavior even for large deposition rates. To get at the more subtle behavior of the non-Bravais, hexagonal system, we turn to examining the meandering, or Bales-Zangwill [5], instability, which strongly couples the morphology of the film to the surface energy. This instability occurs in systems with a large step-edge, or Ehrlich-Schwoebel [6,7], barrier that inhibits the interlayer motion of diffusing