Interactions between Fluctuating Steps on Vicinal Surfaces: Edge Energy Effects in Reconstruction Induced Faceting

Da-Jiang Liu[1] and John D. Weeks[1,2]
[1]*Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742*
[2]*Department of Chemistry, University of Maryland, College Park, Maryland 20742*
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Surface reconstruction can generate effective attractive interactions between steps on vicinal surfaces, leading to the formation of step bunches. Modified repulsive interactions arise from the fluctuations of a step in the asymmetric environment at the edge of the step bunch. These are determined by a mapping to the ground state energy of a quantum particle between two rigid walls in an external field. This yields an edge energy term that controls the dynamics of faceting and causes wider step spacings at the edge of the bunch, in agreement with Monte Carlo simulations. [S0031-9007(97)03948-3]

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Theories used to explain step morphology and dynamics on vicinal surfaces often relate the velocity of a step to changes in the local surface free energy expressed as a functional of the step positions [1,2]. Constraints on possible transverse step fluctuations arise because of the prohibitive energy cost arising from step overhangs. This gives rise to an effective entropic repulsive interaction between steps at nonzero temperature that tends to keep steps uniformly spaced [3]. The two-dimensional (2D) terrace-step-kink (TSK) model [4], which can be mapped onto a 1D free-fermion model [5], provides a quantitative description of effects arising from the no-crossing constraint.

A simpler 1D description may be adequate for many vicinal surface problems that exhibit quasi-one-dimensional features. The 1D model can be obtained by averaging the transverse step fluctuations in the 2D TSK model over a mesoscopic distance L_y along the step edge direction, expressing the effective step interactions in terms of the *average* positions of the steps. Rettori and Villain [6] proposed a 1D *local* free energy model for surfaces with nonuniform step spacings, summing separate contributions from each terrace, or equivalently, from individual steps with effective repulsive interactions between nearest-neighbor (NN) *pairs* of steps only. In the 1D NN approximation, the effective step pair interaction must vary as $1/w^2$, with w the average width of the terrace separating them, so that the known results for the equilibrium free energy of a uniform vicinal surface [3,5,7] can be recovered. This model and various generalizations have proved very useful in a number of different applications [8–12].

However, the simple NN description fails to describe some essential features of the physics in certain cases where competing interactions exist that favor very nonuniform step configurations. We study here one such example, the reconstruction induced "phase separation" into wide reconstructed facets and unreconstructed step bunches as seen on vicinal Si(111) and many other surfaces [13–15].

While reconstruction can lower the free energy of a flat terrace on which it occurs, it generally makes defects such as steps that disturb the reconstruction energetically more costly [3,16]. This suggests that reconstruction should occur on a stepped surface only for sufficiently wide terraces above some "critical" terrace width w_c, as seen in many experiments [11,13,14]. To take account of this physics, we use a simple *two state critical width model* [10], which assumes that each terrace region is either reconstructed or unreconstructed, depending only on the local terrace width. This model seems particularly appropriate when steps are "stiff," with reconstruction occurring more rapidly than the step movements, and when the average step spacings are smaller than or on the order of the size of the critical nucleus for growth of reconstruction on the flat surface. We will use this idea in the TSK model to yield a microscopic 2D model incorporating both reconstruction and entropic confinement effects, as discussed below. However, for faceted surfaces with relatively straight steps but widely differing terrace spacings, a 1D treatment may suffice.

To that end, let us describe the energetics for reconstruction on the surface as the sum of energies from each terrace in the form

$$E(w) = (f_r^0 w + \beta_r)\Theta(w - w_c) + (f_u^0 w + \beta_u)\Theta(w_c - w)$$
$$= f_r^0 w + \beta_r - \epsilon_r(w_c - w)\Theta(w_c - w). \quad (1)$$

Here $f_{r(u)}^0$ is the free energy density of a flat terrace, $\beta_{r(u)}$ is the creation energy per unit length of an isolated step when the surface is completely reconstructed (unreconstructed), and $\Theta(w)$ is the Heaviside step function. Both the flat surface energy gain $\epsilon_r \equiv f_u^0 - f_r^0$ and the step energy cost $\epsilon_s \equiv \beta_r - \beta_u$ on reconstruction should be positive for phase separation to occur; the critical terrace width w_c above which reconstruction is favored is given by $w_c \equiv \epsilon_s/\epsilon_r$ in this model. Since the total terrace area and number of steps are conserved for vicinal surfaces, the first two terms on the right-hand side of Eq. (1) contribute only a constant to the total energy when summed

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over all terraces and will be ignored in what follows. In effect, we measure the reconstruction component of the energy relative to that of a surface in which every terrace is reconstructed. Thus reconstruction effects generate an effective negative (*attractive*) interaction proportional to $w_c - w$ between pairs of steps with spacing $w < w_c$.

The simplest treatment [10] incorporating both reconstruction and the step repulsions adds to $E(w)$ the repulsive term g/w^2 as in the Rettori-Villain model above. The total free energy functional is then a sum of effective interactions

$$V^{\mathrm{NN}}(w) \equiv E(w) + g/w^2 \tag{2}$$

between NN pairs of steps. This simple NN model has been applied successfully in several cases [10,11] and has many appealing features: it reduces to the exact Gruber-Mullins form [7] for the free energy of a uniform vicinal surface, and it correctly reproduces the thermodynamics of phase separation into macroscopic regions with facets and step bunches.

However, a more careful treatment of the interplay between reconstruction and the repulsive interactions is required to understand important aspects of the coarsening dynamics and the step spacings in a bunch. While it seems reasonable to treat the reconstruction energy $E(w)$ on a local terrace-by-terrace basis as in Eq. (1), the effective entropic repulsions have a very different origin. These arise from the constraints on possible transverse fluctuations of a given step from *both* its neighbors due to the no-crossing condition. When transverse fluctuations of a step occur in a very asymmetric environment, such as that encountered at the boundary between a step bunch and a facet, their distribution is quite different from that found when a step is in a symmetric environment like the middle of a bunch. This generates additional nonlocal contributions to the free energy ignored by the NN approximation that turn out to have important consequences.

Since many essential features arising from asymmetric fluctuations can be captured by a model with only three steps, we assume the local free energy depends on the positions of *three adjacent steps* rather than *pairs* as in the NN model. The total free energy of a system with N_s steps can thus be written as

$$F = L_y \sum_{n=1}^{N_s} \mathcal{L}(x_{n-1}, x_n, x_{n+1}) + F_0, \tag{3}$$

where F_0 is a constant and $\mathcal{L}(x_{n-1}, x_n, x_{n+1})$ describes a general *three-step* interaction between step n with average position x_n and both its nearest neighbors at average positions x_{n-1} and x_{n+1}. Following Gruber and Mullins [7], we approximate the effect of the no-crossing condition on the fluctuations of step n by two hard walls at x_{n-1} and x_{n+1}. However, we consider the general *asymmetric* case where the average position of step n is *specified* as some particular x_n, differing in general from the unconstrained symmetric value $\bar{x}_n = (x_{n-1} + x_{n+1})/2$. In practice, it is easier to generate this asymmetry by using a grand canonical picture, with step n coupled to a conjugate linear external field h of appropriately chosen strength, rather than by directly imposing the constraint of a fixed average position x_n.

The transfer matrix description of step fluctuations [7] leads to a well known mapping [5] to the properties of a 1D quantum particle that satisfies the time-independent Schrödinger equation

$$\left[-\frac{\hbar^2}{2m_e}\frac{d^2}{dx^2} + \Phi(x \mid x_1, x_3)\right]\psi_0(x) = E_0\psi_0(x), \tag{4}$$

where m_e is the effective mass (controlling the stiffness of the step), and $\psi_0(x)$ and E_0 are the ground state wave function and energy, respectively. $\Phi(x \mid x_1, x_3)$ is the potential field for the quantum particle. It incorporates the following ingredients: two infinite hard walls [17] at x_1 and x_3, the energy change from reconstruction, and the linear external field. Using Eq. (1), we can write

$$\Phi(x \mid x_1, x_3) = [V^d(x - x_1) + V^d(x_3 - x)]/2 + hx, \tag{5}$$

where $V^d(w) = \infty$ for $w < 0$, and otherwise has the form

$$V^d(w) = -\epsilon_r(w_c - w)\Theta(w_c - w). \tag{6}$$

The average position of the fluctuating step can be obtained by $x_2 = \int x\psi_0^2(x)\,dx$. The presence of the external field h will shift x_2 away from the center. Since x_2 is a monotonic function of h, we can express h as a function of x_2. When $L_y \to \infty$, the appropriate "intrinsic" free energy in terms of step positions is given by the following Legendre transformation:

$$\mathcal{L}(x_1, x_2, x_3) = E_0(x_1, x_3; h(x_2)) - x_2 h(x_2). \tag{7}$$

We can solve for $\mathcal{L}$ either numerically or analytically.

Even in the absence of reconstruction effects (i.e., as $\epsilon_r \to 0$), $\mathcal{L}$ obtained in this way differs quantitatively from the predictions of the NN model, where from Eq. (2),

$$\mathcal{L}^{\mathrm{NN}}(x_1, x_2, x_3) = [V^{\mathrm{NN}}(x_2 - x_1) + V^{\mathrm{NN}}(x_3 - x_2)]/2. \tag{8}$$

For convenience, we define $\omega = (x_3 - x_1)/2$ as the average terrace width and $\tilde{\sigma} \equiv (2x_2 - x_1 - x_3)/2\omega$ as the relative shift of the middle step. Rewriting Eq. (4) in terms of these variables, we see that as $\epsilon_r \to 0$, $\mathcal{L}$ can be expressed in the scaling form: $\mathcal{L}(x_1, x_2, x_3) \sim \omega^{-2}\phi(\tilde{\sigma})$. Similarly, the NN approximation gives $\mathcal{L}^{\mathrm{NN}}(x_1, x_2, x_3) \sim \omega^{-2}\phi^{\mathrm{NN}}(\tilde{\sigma})$, with a different scaling function ϕ^{NN}. Normalizing so that both functions have the same dependence on the average width when $\tilde{\sigma} = 0$, we find that the quantum mechanical scaling function increases more rapidly than the simple NN approximation as $\tilde{\sigma}$ deviates from zero. As $\tilde{\sigma} \to 0$, $\phi(\tilde{\sigma}) = 1 + 5.771\tilde{\sigma}^2$, while $\phi^{\mathrm{NN}}(\tilde{\sigma}) = 1 + 3\tilde{\sigma}^2$. As $\tilde{\sigma} \to 1$, $\phi(\tilde{\sigma}) = 0.7674/(1 - \tilde{\sigma})^2$, and $\phi^{\mathrm{NN}}(\tilde{\sigma}) = 0.5/(1 - \tilde{\sigma})^2$. These differences,

while conceptually important, produce only relatively small quantitative corrections to most predictions of the simple NN approximation in the absence of a driving force producing very nonuniform configurations.

However, in the presence of reconstruction effects, the differences become much more significant. First we take $h = 0$ and look at the symmetric ground state energy of the quantum particle in the presence of the potential (5) from reconstruction. Figure 1 plots $E_S(\omega) \equiv E_0(\omega, h = 0)$ for different ϵ_r and a *fixed* w_c. When the entropic repulsions dominate (at small ϵ_r), this will decrease monotonically as ω increases and have its minimum value at $\omega = \infty$. However, there is a critical value for ϵ_r above which $E_S(\omega)$ has its minimum at a *finite* width $\omega_{\min}$. We can interpret $E_S(\omega)$ as the metastable Helmholtz free energy, expressed here as a function of ω rather than the slope $s = 1/\omega$ as is the usual practice [13]. When ϵ_r is larger than the critical value, it is favorable for the system to phase separate, with coexistence of an unreconstructed step bunch with average terrace width $\omega_{\min}$ and a reconstructed flat terrace. Similar results have been shown by Burkhardt [18] in systems with a square well potential V^d.

The free energy for nonuniform step configurations can be obtained by applying the external field h. For small shifts $\sigma \equiv x_2 - (x_1 + x_3)/2$ away from the center, $\mathcal{L}$ is quadratic in σ with a coefficient g_1 satisfying

$$\mathcal{L}(\omega, \sigma) \approx E_S(\omega) + g_1\sigma^2/2. \tag{9}$$

If we impose a small perturbation on the positions of steps in a uniform 1Dstep train with spacing ω_0, the change in the total free energy is

$$\Delta F \approx \frac{1}{2}\sum_q [2g_0(1 - \cos q) + (g_1 - g_0)(1 - \cos q)^2]|u_q|^2, \tag{10}$$

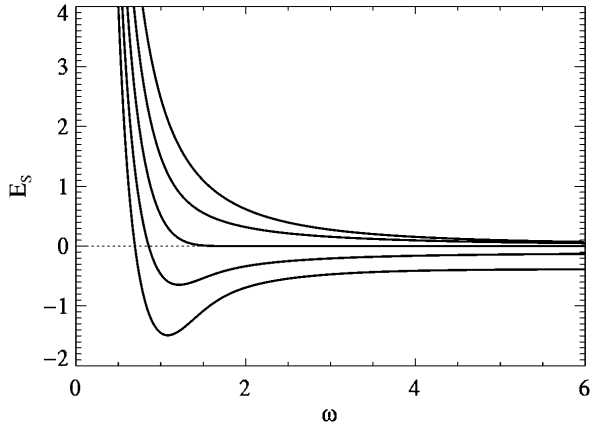

FIG. 1. The dependence of the ground state energy on the average width for different ϵ_r with fixed $w_c = 2$. From top to bottom the value for ϵ_r is 0, 1/2, 1, 3/2, 2 times the critical value.

to leading order in the displacements u, where $u_m \equiv x_m - m\omega_0 = N_s^{-1/2}\sum_q u_q e^{iqm}$ and

$$g_0 = \partial^2 E_S(\omega)/\partial\omega^2|_{\omega=\omega_0} \tag{11}$$

For small q, the coefficient g_0 of the q^2 term in Eq. (10) measures the resistance or stiffness of the step train to long wavelength changes in its spacings. Note from Fig. 1 that this *decreases* as ϵ_r increases [19]. The inflection point, given by $g_0 = 0$, describes the *spinodal* in the classical theory for phase separation.

One of the most important predictions of the quantum calculation is that there is a nonzero value for the term $(g_1 - g_0)(1 - \cos q)^2$ in Eq. (10). This term plays a role analogous to the square gradient term in the Cahn-Hilliard free energy functional for liquid-vapor phase separation, and to the *edge energy* (or *corner energy* by some authors) in continuum models for surface dynamics [20]. It increases as q^4 for small q and reaches its maximum for $q = \pi$ (the step pairing mode). The NN approximation from Eq. (8) predicts that $g_1 = g_0$ for *any* pair potential V^{NN}, and hence sets this term to zero. As a result, *all* modes are unstable when $g_0 < 0$, with the step pairing mode most unstable. The quantum mechanical calculation using the potential in Eq. (5) gives $g_1 > g_0$. Thus, unlike the NN approximation, a negative stiffness g_0 does not necessarily yield negative energies for short wavelength perturbations. This provides one possible explanation for the wavelength selection experimentally observed in the spinodal regime [16].

Another important application of the new free energy functional is to the spacing of steps in the step bunch induced by reconstruction. Because of the neglect of edge energy effects, the NN approximation predicts that all terraces in the bunch have the same width, while the quantum free energy functional predicts *wider* step spacings at the edge of the bunch. It may be possible to test this prediction experimentally.

To provide a theoretical test, we carried out Monte Carlo (MC) simulations of a generalized 2D TSK model. The system consists of M steps, each having N_y segments. Steps with average orientation in the y direction are modeled by the absolute solid-on-solid model with kink energy ϵ. Interactions between steps are through segments at the same y position only. Each segment interacts with its nearest neighbors using $V^d(w)$ in Eq. (6). We attempt to move random segments forward or backward in the x direction for one lattice unit; the move is rejected or accepted using the Metropolis algorithm. When ϵ_r is large enough, the system facets into flat reconstructed terraces and an isolated step bunch. In Fig. 2 we show (in diamonds) the average widths of each of the terraces in an isolated bunch of eight steps. The dashed line is the result from numerically minimizing the total free energy of a 1D step train using the three-step interactions. The effective mass m_e in Eq. (4) was chosen to give the same terrace

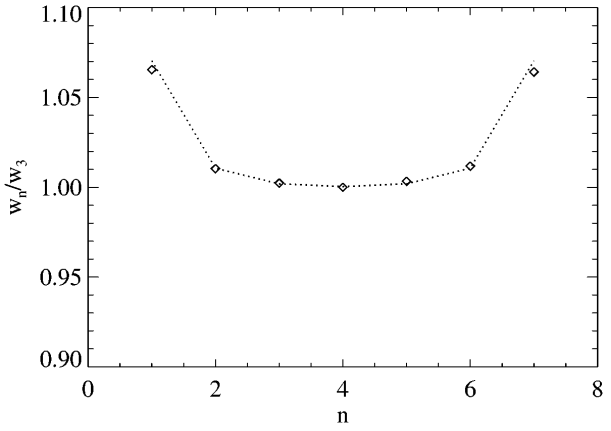

FIG. 2. The relative average terrace widths of a step bunch from the numerical simulation (diamonds) and from the minimization of the free energy functional (dashed line). $M = 8$, $N_y = 4096$, $\epsilon = 1k_BT$, $w_c = 10$, and $\epsilon_r = 0.16k_BT$. The relative widths are insensitive to the parameters as long ϵ_r much larger than the critical value.

width in the middle of the bunch as that from the MC simulation. The theory predicts an increase in the terrace widths near the edge of the bunch in excellent agreement with the simulations.

In conclusion we have estimated the effective interactions between steps in the 1D step model of vicinal surfaces using a simple quantum mechanical approximation. Application to the phase separation problem on vicinal surfaces predicts an *edge energy* associated with the boundary between two phases, a 1D analog to the interface free energy in liquid-vapor phase separation. As was shown by Stewart and Goldenfeld [20] in their continuum model, the edge energy is essential to many features of the phase separation. This is the first quantitative estimation of the edge energy based on a reasonable microscopic model treating steps as the fundamental unit. Although other physical effects (e.g., different bonding configurations at the edge of a step bunch) might be present and could contribute significantly to the edge energy in some specific systems, the step fluctuations are ubiquitous and can serve as a generic source for the edge energy.

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