Facet Ridge End Points in Crystal Shapes

Douglas Davidson and Marcel den Nijs
Department of Physics, University of Washington, P.O. Box 351560, Seattle, Washington 98195-1560
(Received 30 June 1999)

We study equilibrium crystal shapes (ECS) near facet ridge end points (FRE) by means of a numerical study of a body-centered solid-on-solid model on a square lattice with an enhanced uniaxial interaction range. This tests the stability of the so-called stochastic FRE point where the model maps exactly onto one dimensional Kardar-Parisi-Zhang-type growth and where the local ECS is simple. We find that the generic shapes are more complex. They contain first-order faceted to rough boundaries terminating in Pokrovsky-Talapov-type end points, and first-order ridges inside the rounded part of the ECS where two rough surface orientations coexist.

PACS numbers: 68.35.Bs, 64.60.Fr, 64.60.Ht, 68.35.Rh

Equilibrium crystal shapes (ECS) have been studied over the span of many years [1]. Many features of their thermal evolution are theoretically well understood and have been observed experimentally. For example, surface roughening of facets are realizations the Kosterlitz-Thouless transition [1]. They have been observed in helium crystals [2], metal surfaces [3], ionic solids [4], and organic crystals [5]. Smooth boundaries between flat facets and rounded rough regions, as in Fig. 1(a), belong to the so-called Pokrovsky-Talapov (PT) universality class. They have been observed in, e.g., lead [6] and helium crystals [7]. An aspect for which experimental data are still sparse is the ECS structure near a facet ridge end point (FRE). For example, in NaCl crystals, facet ridges seem to vanish very quickly as temperature is increased [8]. Many other experiments reproduce nonequilibrium (so-called growth) shapes, where FRE points are not represented properly (rough surface orientations are suppressed because they grow faster than facets).

Lately the ECS structure near FRE points has gained theoretical attention, with the discovery of a link with Kardar-Parisi-Zhang(KPZ)-type nonequilibrium growth [9]. Figure 1(a) represents the simplest and until now canonical ECS structure near FRE points. The sharp ridge between two faceted orientations terminates and splits into two PT facet-to-round boundaries. This structure is realized in the so-called body-centered solid-on-solid (BCSOS) model with next-nearest neighbor interactions only [10], which is equivalent to the exactly solved six-vertex model. The ECS near the FRE point has a conical shape where a continuum of coexisting surface orientations come together [10]. Moreover, this FRE point can be mapped exactly onto a one dimensional BCSOS growth model that lies in the KPZ universality class [9]. To be more precise, the transfer matrix of the two dimensional equilibrium model maps onto the master equation of the one dimensional growth model. The spatial direction parallel to the facet ridge plays the role of time in the dynamic process [9,11].

This seems to settle the issue, but the FRE point in this exactly soluble model has too much symmetry (by being stochastic) to leave us confident that its scaling behavior is universal and that the ECS of Fig. 1(a) represents the generic shape. The stochastic nature of the transfer matrix implies that the free energies of all surface orientations in the faceted direction are degenerate at the FRE point. This is a highly nongeneric and accidental property of this specific model. Recently, we performed a study of the ECS in a BCSOS model on a honeycomb lattice [11]. There we did not find the structure of Fig. 1(a), but instead shapes equivalent to Figs. 1(b) and 1(c). In (b) the facet ridge extends into the rough region as a first-order rough-to-rough (FOR) line. It

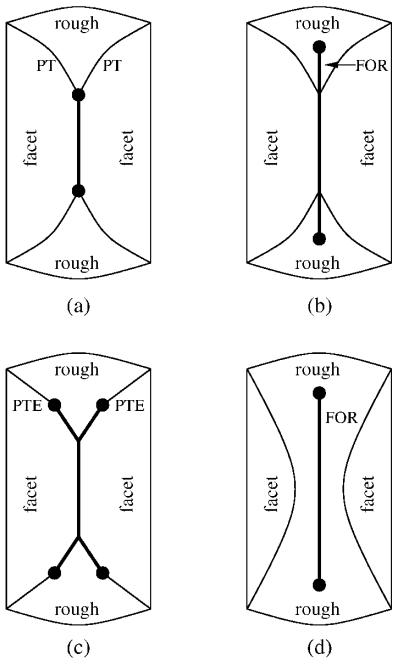

FIG. 1. Equilibrium crystal shapes in the BCSOS model with enhanced interaction range: (a) ECS in the exactly soluble square lattice BCSOS model with stochastic FRE point. (b) ECS with a first-order line extending into the rough area. (c) ECS with first-order facet-to-round boundaries and PTE points. (d) ECS with a spontaneous tilted rough phase, i.e., with a first-order ridge inside the rough phase.

 0031-9007/00/84(2)/326(4)$15.00

terminates at a critical end point. This possibility had been suggested before [10] but had not been observed in any model beyond mean field theory. Our result was somewhat unsatisfactory, however, since the FOR line remained extremely short. In another part of the phase diagram we found an ECS similar to Fig. 1(c). The boundaries between the faceted and the rounded rough regions are partially first order. These segments became quite long and we could establish the scaling behavior of the critical end points (PTE points) where the transition becomes PT-like. PTE scaling is in agreement with a simple theory where the free energy is assumed analytic on the rough side and expandable in powers of the tilt angle [11–13]. PTE points have been observed in Si(113) [14], but with scaling exponents different from the above mean field-type values. This can be attributed to long range attractive step-step interactions in the context of step bunching [13,15].

Here, we present a study of the BCSOS model on the square lattice with enhanced interaction range, to address directly the stability of the stochastic FRE point. The FOR lines are well developed in this model. They appear also as stand-alone ridges inside the rounded parts of the crystal, as shown in Fig. 1(d), representing spontaneous symmetry breaking within the rough phase (coexistence between two rough surface orientations).

Consider a square lattice, oriented diagonally. The most general Hamiltonian with only next-nearest neighbor interactions can be written as

$$H_0 = \sum_{x,y} [\tfrac{1}{4} L_H (h_{x+2,y} - h_{x,y} - E_H/L_H)^2 + \tfrac{1}{4} L_V (h_{x,y+2} - h_{x,y} - E_V/L_V)^2] \qquad (1)$$

with $x+2, y$ $(x, y+2)$ and x, y next-nearest neighbors in the horizontal (vertical) direction and $h_{x,y} = 0, \pm 1, \pm 2, \ldots$ the height variables. Nearest neighbor heights must differ by one. All energies are in dimensionless units of $k_B T$. E_H and E_V couple to the slopes, which we denote as Q_H and Q_V, respectively. In this diagonal setup, the timelike direction of the transfer matrix coincides with the facet ridges in Fig. 1. The ECS of this model takes the structure of Fig. 1(a) when $\exp(-L_H) > \exp(-L_V) + 1$, in particular, when the step-step interactions are attractive in the horizontal direction and repulsive in the vertical direction. The FRE point has the stochastic exactly soluble KPZ character mentioned above [9,10].

The stability of the stochastic FRE point can be studied by increasing the interaction range. They break the special symmetries of H_0. For numerical convenience, we choose the following uniaxial interactions between next-to-next-nearest neighbors lying in the same horizontal row:

$$H = H_0 + \sum_{x,y} [M_2 \delta(h_{x,y}, h_{x+4,y} \pm 2) + M_4 \delta(h_{x,y}, h_{x+4,y} \pm 4)] \qquad (2)$$

with $\delta(x)$ Kronecker delta's. This involves two coupling constants, M_2 and M_4, because those farther neighbors can differ in height by 0, ± 2, or ± 4. The details of the numerical analysis are the same as in our previous paper [11]. The eigenvalues of the transfer matrix yield the exact free energy as function of tilt angle, $f(E_V, Q_H, N)$, at specific temperatures in a semi-infinite strip geometry of width N. The ECS follows from this by a $N \to \infty$ finite size scaling analysis, combined with a Legendre transform. The latter is in essence the Wulff construction [16].

The phase diagram at $L_H = -0.69$ and $L_V = 0.69$ for zero tilt fields, $E_H = E_V = 0$, is shown in Fig. 2. This is a representative example. In the upper right corner, where M_2 and M_4 are both large and positive, the surface is flat. As M_4 is decreased, the surface undergoes a first-order transition to a faceted phase. The slope of the surface changes abruptly from $(0, 0)$ to two coexisting $(Q_H, Q_V) = (\pm 1, 0)$ facets. As M_2 is decreased, starting from the flat phase, the surface first roughens, via a Kosterlitz-Thouless (KT) transition and then enters a spontaneously tilted rough phase [17]. This is a rough-to-rough faceting transition with yet unknown anisotropic scaling properties. In the tilted phase, two rough phases coexist. The rounded part of the ECS contains a first-order ridge as shown in Fig. 1(d). The jump in orientation is caused by the competition between the L and M interactions and changes continuously throughout this phase. It locks in smoothly to $Q_H = \pm 1$ at the PT boundary into the faceted phase.

The dashed line in Fig. 2 inside the faceted phase does not represent a phase transition. It marks the boundary between the shapes of Figs. 1(b) and 1(c). In region (c), the edge between each facet and the rounded rough region is sharp near the FRE point. The scaling at the PTE point (where the edge becomes a conventional PT boundary) is consistent with an analytic free energy functional in terms of the surface tilt angle. The correlation length in the direction along the facet ridge

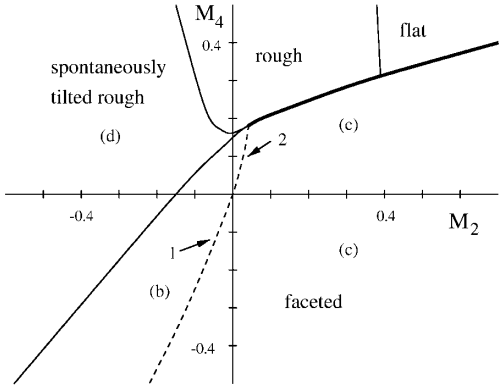

FIG. 2. Phase diagram of the model of Eq. (2) for $L_H = -0.69$ and $L_V = 0.69$, at $E_H = E_V = 0$. The labels (b), (c), and (d) refer to the ECS in Fig. 1, and 1 and 2 to Figs. 4(a) and 4(b).

scales compared to the perpendicular one as $\xi_{\parallel} \sim l_{\perp}^{z}$ with $z = 3$ [11–13].

In region (b) the first-order facet ridge boundary between the $(\pm 1, 0)$ facets extends into the rounded region as a FOR line, as shown in Fig. 1(b). Unlike our previous study on the honeycomb lattice [11], the FOR line becomes quite long and is unambiguously resolved. For example, at point $(L_H, L_V, M_2, M_4) = (-0.69, 0.69, -0.02, 0.02)$ the end point of the FOR line lies at $E_V = 1.04 \pm 0.01$, while the location of the FRE point is known exactly, $E_V = 0.908$. At the phase boundary into the spontaneously tilted rough phase, the ECS changes from Fig. 1(c) to Fig. 1(d). In the latter the facet-to-round boundary never touches the FOR line.

The scaling behavior at the FOR end point is an important issue. A naive guess is to assume the free energy is analytic in terms of the tilt angles, i.e., the asymptotic form $f(Q_H, E_V) = A(E_V - E_V^*)Q_H^2 + BQ_H^4$, such that at the FOR critical end point the free energy scales like $f \sim Q_H^4$. The free energy gap between the $Q_H = 0$ and $Q_H = 1/L$ sectors would behave as $L[f(1/L) - f(0)] \sim L^{-3}$, which translates into an anisotropic scaling exponent $z = 3$. The latter is inconsistent with our numerical data. Figure 3 illustrates the finite size scaling estimates for z at two FOR end points, located, respectively, at $E_V = 1.05$ for $(L_H, L_V, M_2, M_4) = (-0.69, 0.69, -0.02, 0.02)$, and at $E_V = 0.62$ for $(L_H, L_V, M_2, M_4) = (-0.41, 0.69, 0.05, -0.05)$. We measure the largest and second largest eigenvalues, λ_0 and λ_1, in the transfer matrix sector with periodic boundary conditions. The gap $m = \ln(\lambda_0/\lambda_1)$ scales with system size like $m \sim N^{-z}$. Figure 3 illustrates that the finite size scaling values of z are rather sensitive to the estimate of the location of the end point and that corrections to scaling vary strongly throughout the phase diagram, but z is clearly smaller than 2. Therefore, the above naive description is incorrect.

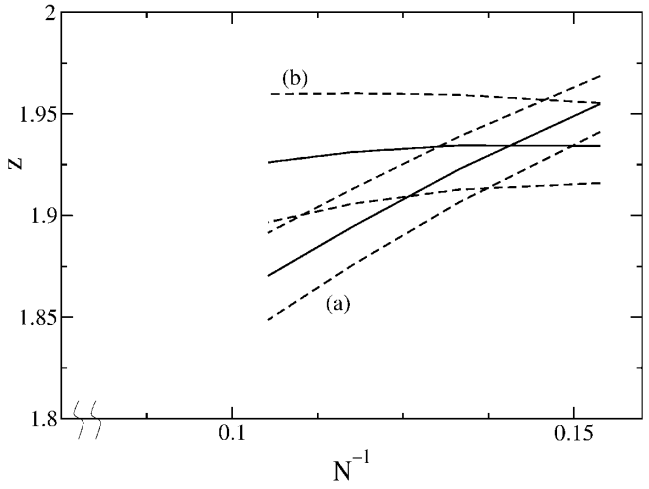

FIG. 3. The effective dynamic exponent as a function of strip width N at the end points of two FOR lines: (a) $(L_H, L_V, M_2, M_4) = (-0.69, 0.69, -0.02, 0.02)$ and (b) $(L_H, L_V, M_2, M_4) = (-0.41, 0.69, 0.05, -0.05)$. The dashed lines represent the uncertainty in the location of the end points.

A second natural guess for the scaling properties of the end points of FOR lines is that they belong to the KPZ universality class. The transfer matrix is not stochastic, but maybe some of its properties survive. The numerical data in Fig. 3 do not exclude the KPZ value $z = 1.5$. To test this possibility in more detail, we check for a discontinuity in surface orientation, ΔQ_V, at the end point in the direction along the FOR line. Q_V jumps at the stochastic FRE point in Fig. 1(a). This represents the growth velocity in $1 + 1$ dimensional KPZ dynamics. At the end points of the FOR lines, on the other hand, this discontinuity vanishes as a function of system size N, like $\Delta Q_V \sim N^{-x}$ with $x = 2.2 \pm 0.1$ at all points we checked. The discontinuity in surface tilt along the FOR line in the perpendicular direction, ΔQ_H, acts as order parameter. It vanishes continuously, probably as a power law, $\Delta Q_H \sim |E_V - E_V^*|^{\beta}$. The discreteness in strip width N allows only commensurate rational values for Q_H. This makes an accurate scaling analysis impossible. However, we are confident that $0.3 < \beta < 0.5$.

In Figs. 1(b) and 1(c) the FRE point has first-order characteristics. The crossover between them takes place near dashed lines 1 and 2 in Fig. 2. Only there we can hope to find simple Fig. 1(a)-type structures. Instead we find only more complex crystal shapes. At the stochastic points $M_2 = M_4 = 0$ the crossover is simple. On approach from the (b) side, the FOR line shrinks in length and vanishes completely, followed by the emergence of PTE points out of the FRE point on the (c) side. Below the stochastic point, on approach of the line marked 1 in Fig. 2, the FOR line shrinks rapidly as well, but just before it disappears completely, the PTE points start to emerge already along the two facet-to-round boundaries.

The intermediate ECS shape is a superposition of structures (b) and (c), as shown in Fig. 4(a). Figure 5 shows the free energy as a function of surface tilt Q_H at $E_V = 0.69$ for $(L_H, L_V, M_2, M_4) = (0, 0.69, -0.14, -0.40)$. The crucial feature is the simultaneous presence of a

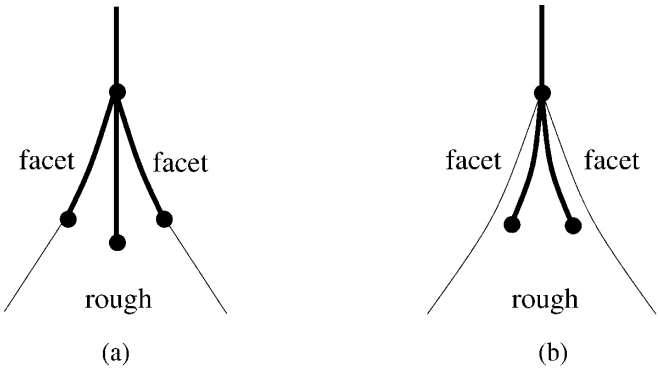

FIG. 4. The ECS near the FRE point in the crossover region between the shapes of Figs. 1(b) and 1(c). (a) Coexistence of the FOR line and PTE points. (b) Splitting of the FOR line.

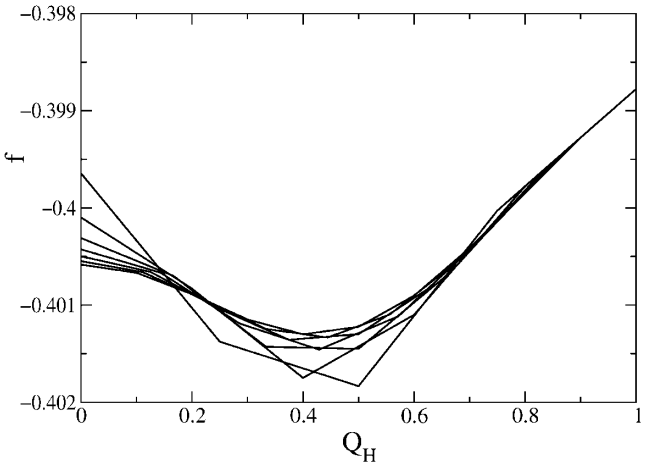

FIG. 5. The free energy as a function of Q_H for $(L_H, L_V, M_2, M_4) = (0.0, 0.69, -0.14, -0.40)$, at $E_V = 0.683$. Only the $Q_H > 0$ side of the mirror symmetric curve is shown. Near $Q_H = 0$, the free energy decreases smoothly with increasing lattice width N.

central maximum at $Q_H = 0$ (followed by two nearby minima; this creates the FOR line) and concavity of the curve at the $Q_H = \pm 1$ edges (the PTE points). Our other paper contains a detailed discussion on how such features translate into ECS properties [11]. The choppiness in Fig. 5 is due to the limitation to rational values of Q_H (multiples of $1/N$). The numbers are known to arbitrary accuracy and their finite size scaling converges smoothly.

This superposition of the FOR and PTE shapes is predictable, because it is hard to imagine how local features of $f(Q_H)$ at opposite tilt angles can be topologically linked to each other, except by special symmetries, like stochasticity. The crossover region is very narrow, but its width is numerically significant. For example, for the values of M_2 and M_4 in Fig. 5, the FRE point lies at $(E_H, E_V) = (0, 0.668 \pm 0.004)$ and the FOR end points at $(0, 0.70 \pm 0.01)$, compared to the virtually exact location $(\pm 0.158\,08, 0.871\,05)$ of the PTE points.

The crossover is more delicate above the stochastic point near line 2 in Fig. 2. The $f(Q_H)$ is globally flatter but at the same time develops extra wiggles and a slightly concave part at intermediate Q_H. First, the FOR line shortens dramatically but then splits; see Fig. 4(b). The two FOR end points rapidly move outwards to merge with the facet-to-round boundary into PTE points. We cannot rule out that this splitting is a finite size scaling artifact. Therefore, we determined also the (effective) anisotropic exponent z, in region 2, pretending the ECS takes the simple form of Fig. 1(a). The results are consistent with the KPZ value $z = 1.5$, but crossover scaling from the stochastic point explains this as well.

In conclusion, the previous canonical picture of equilibrium crystal shapes near facet ridge end points where the facet ridge splits into two PT lines, as in Fig. 1(a), is too naive. We establish that the stochastic FRE point is unstable. The codimension of such FRE points in an even more generalized parameter space must be very low. For the first time we observe FOR lines unambiguously. Such FOR lines and also first-order facet-to-round segments must be common features of experimental equilibrium crystal shapes; i.e., the local equilibrium crystal shapes of Figs. 1(b) and 1(c) and their superposition, Fig. 4(a), must be the generic structures. Standalone FOR lines also realized in our model, i.e., ridges inside the rounded part of the crystal where the surface orientation jumps, as in Fig. 1(d). These ECS features reflect the functional form of the free energy curve $f(Q_H)$, which is completely featureless only at the stochastic FRE point. Everywhere else it retains at least some structure, even in the crossover regions. The crystal shape in Fig. 1(a) is an anomaly.

This research is supported by NSF Grant No. DMR-9700430.

[1] For a review, see C. Rottman and M. Wortis, Phys. Rep. **103**, 59 (1984).
[2] See, e.g., F. Gallet, S. Balibar, and E. Rolley, J. Phys. (Paris) **48**, 369 (1987).
[3] J. C. Heyraud and J. J. Métois, J. Cryst. Growth **82**, 269 (1987).
[4] T. Ohachi and I. Taniguchi, J. Cryst. Growth **65**, 84 (1983).
[5] See L. A. M. J. Jetten, H. J. Human, P. Bennema, and J. P. van der Eerden, J. Cryst. Growth **68**, 503 (1984), and references therein.
[6] C. Rottman, M. Wortis, J. C. Heyraud, and J. J. Métois, Phys. Rev. Lett. **52**, 1009 (1984).
[7] Y. Carmi, S. G. Lipson, and E. Polturak, Phys. Rev. B **36**, 1894 (1987).
[8] J. C. Heyraud and J. J. Métois, J. Cryst. Growth **84**, 503 (1987).
[9] J. Neergaard and M. den Nijs, Phys. Rev. Lett. **74**, 730 (1995).
[10] J. D. Shore and D. J. Bukman, Phys. Rev. Lett. **72**, 604 (1994); Phys. Rev. E **51**, 4196 (1995).
[11] D. Davidson and M. den Nijs, Phys. Rev. E **59**, 5029 (1999).
[12] V. B. Shenoy, S. Zhang, and W. F. Saam, Phys. Rev. Lett. **81**, 3475 (1998).
[13] We do not have enough sensitivity to see the logarithmic factor predicted by S. M. Bhattacharjee, Phys. Rev. Lett. **76**, 4568 (1996).
[14] S. Song and S. G. J. Mochrie, Phys. Rev. Lett. **73**, 995 (1994); Phys. Rev. B **51**, 10 068 (1995).
[15] M. Lässig, Phys. Rev. Lett. **77**, 526 (1996).
[16] A. F. Andreev, Sov. Phys. JETP **53**, 1063 (1981).
[17] The precise location of these transitions is obscured by modulations in $f(Q_H)$ that occur only in this part of the phase diagram. The transition between the rough and tilted rough phases may be partially first order.