Roughening and Facet Formation in Crystals

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For a large class of models, the connection between roughening and facet formation is explored in detail. It is shown that there is a universal jump in the crystal surface curvature at the roughening transition. Explicit calculations within one model yield facet shapes and a universal exponent describing crystal shapes near a facet. Hyperscaling arguments provide facet sizes for generalized solid-on-solid models.

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In this Letter we address the problem of the formation of facets in crystals. Within a particular model we provide the first exact calculation of facet shapes in three-dimensional crystals. The connection between roughening[1] and faceting is delineated and it is shown that at the faceting transition temperature T_R (signaled by the appearance of a flat face on a smoothly curved crystal surface) there is a universal (discontinuous) jump in the surface curvature within a large class of models. Below T_R the shape near the facet edge is governed by a universal exponent. Both these results should be testable experimentally.

A mean-field theory of facet formation has been proposed by Andreev.[2] The connection between roughening and faceting follows from van Beijern's[3] comment that the step free energy[4] vanishes at the roughening transition. This connection is made more explicit by Cabrera and Garcia[5] who combine van Beijern's results with a mean-field-like approach to analyze ^{4}He crystal shapes below T_R. Andreev's theory yields step energies (and hence facet sizes) which are in serious disagreement with van Beijern's results. Cabrera and Garcia's phenomenological approach yields, as we will show, an incorrect shape near the facet edge. In the following, the connection between roughening and crystal shapes is precisely explored within a class of solid-on-solid (SOS) models.

Our explicit calculations are performed for the body-centered solid-on-solid (BCSOS) model studied in Ref. 3. We also demonstrate, using standard duality arguments, that generalized SOS models exhibit precisely the same jump in surface curvature as the specific BCSOS model. This jump is universal in appropriately scaled units in analogy with the jump in the superfluid density in two dimensions.[6] Hyperscaling arguments for the SOS models predict facet sizes in agreement with the BCSOS model computations.

Crystalline shapes (for macroscopic systems) are determined by the Wulff construction.[7] This construction follows from the minimization of the surface free energy subject to the constraint of constant volume, i.e., we minimize

$$\int dx\, dy[f(\vec{\mathrm{h}}) - 2\lambda z(\vec{\mathrm{x}})]\,. \tag{1}$$

Here we have chosen coordinates x, y, z with the origin at the center of the crystal, whose surface is given by $z(\vec{\mathrm{x}}) \equiv z(x,y)$ $[\vec{\mathrm{x}} = (x,y)]$, and $\vec{\mathrm{h}} = \nabla z(\vec{\mathrm{x}})$. Also, $f(\vec{\mathrm{h}}) = \alpha(\vec{\mathrm{h}})(1 + |\vec{\mathrm{h}}|^2)^{1/2}$, where $\alpha(\vec{\mathrm{h}})$ is the surface tension, and 2λ is the Lagrange multiplier. The solution to the variational problem posed by (1) is expressed most conveniently in terms of the Legendre-transformed potential

$$\tilde{f}(\vec{\eta}) = \min_{\vec{\mathrm{h}}} [f(\vec{\mathrm{h}}) - \vec{\eta}\cdot\vec{\mathrm{h}}]\,, \tag{2}$$

where $\vec{\eta} \equiv \partial f/\partial \vec{\mathrm{h}}$. As Andreev emphasizes, the equilibrium crystal shape is given by

$$\lambda z(\vec{\mathrm{x}}) = \tilde{f}(-\lambda\,\vec{\mathrm{x}})\,, \tag{3}$$

the most useful form of the Wulff construction for our purposes.

We consider first the calculation of crystal shapes [Eq. (3)] within the BCSOS model. This is a model for the (100) face of a body-centered cubic crystal which excludes voids and overhangs (the solid-on-solid condition). As van Beijern[3] shows, this model is simply mapped onto a special case of the six-vertex model,[8] the so-called F model. The mapping is illustrated in Fig. 1. The filled circles represent atoms in the top layer of a cubic lattice, while the open circles represent atoms one-half layer down in the body-centered positions. A minus sign indicates that an atom is missing (but those directly below it are not). The arrows follow conventional notation[8] for the vertices of the six-vertex model. Only in-plane bond energies appear explicitly and they are assigned energy $-J$. The electric

polarizations x and y of the six-vertex model correspond, respectively, to $-\sqrt{2}\,h_y$ and $+\sqrt{2}h_x$ in our notation. The horizontal and vertical electric fields h and v correspond to $-\eta_y A/\sqrt{2}$ and $\eta_x A/\sqrt{2}$, respectively, where A is the unit-cell area for the model as given in Fig. 1. The field dependence of the vertex energies is indicated in Fig. 1. Knowledge of the six-vertex-model free energy as a function of h and v thus permits computation of the crystal shape via Eq. (3). Fortunately, Sutherland, Yang, and Yang[9] (SYY) have given relevant results for the free energy.

We first examine the case $T \geq T_R$, where $k_B T_R = J/\ln 2$ is the roughening temperature at $\vec{\eta} = 0$. From the results of SYY, Eq. (3) becomes, for small x and y,

$$\lambda z(x,y) = f_0 - d^2(\lambda^2 x^2 + \lambda^2 y^2)/(\pi - \mu)k_B T, \qquad (4)$$

where $\cos\mu = \frac{1}{2}\exp(2J/k_B T) - 1$, f_0 is the zero-field free energy per unit area, and d is the distance between lattice planes. The curvature of the surface, $\kappa \equiv |\partial^2(\lambda z)/\partial(\lambda r)^2|$, where $r = x^2 + y^2$, is thus

$$\kappa = 2/(\pi - \mu)\kappa_B T. \qquad (5)$$

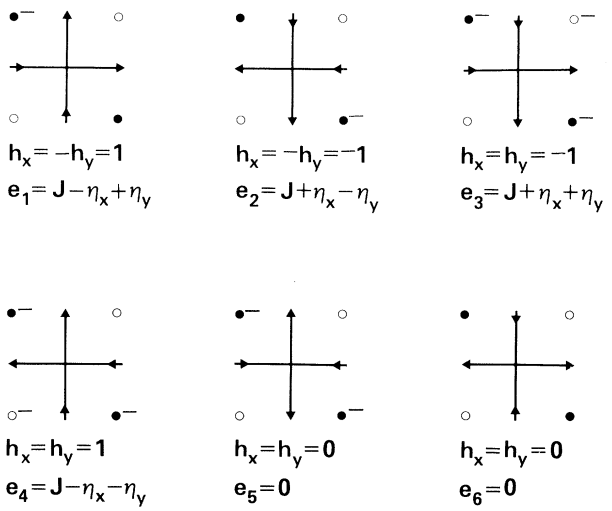

FIG. 1. Correspondence between the BCSOS and six-vertex models. J is the coupling between atoms in the same plane, the h_i are local surface slopes, the η_i are fields coupled to the slopes, and the e_i are vertex energies. Note that the six-vertex-model axes are rotated by 45° from the natural axes of the (100) crystal face. Correspondence with the text is achieved by the replacements $h_i \to \sqrt{2}h_i$ and $\eta_i \to \eta_i A/\sqrt{2}$.

As $T \to T_R^+$, $\kappa \to 2d^2/\pi k_B T_R$, a finite value in contrast to the theory of Andreev[2] where $\kappa \sim T - T_R$ at the transition.

For $T < T_R$ the results of SYY translate to $\lambda z(\vec{x}) = f_0(T)$, a constant in a region in $(\lambda x, \lambda y)$ space bounded by the closed curve

$$A\lambda x = -k_B T\sqrt{2}\,Z(\omega + \varphi), \quad A\lambda y = -k_B T\sqrt{2}\,Z(\varphi), \qquad (6)$$

where $-2\omega \leq \varphi \leq 2\omega$, $2\cosh\omega = \exp(2J/k_B T) - 2$, and

$$Z(\varphi) = \ln\frac{\cosh\frac{1}{2}(\omega + \varphi)}{\cosh\frac{1}{2}(\omega - \varphi)} - \frac{1}{2}\varphi - \sum_{n=1}^{\infty}\frac{(-1)^n e^{-2n\omega}\sinh n\varphi}{n\cosh n\omega}. \qquad (7)$$

Equation (7) thus provides the facet shape for $T < T_R$. Note that the curvature jumps discontinuously from $2d^2/\pi k_B T_R$ to zero at $T = T_R$. Precisely the same jump occurs for the generalized SOS model, as we show later; the jump (in units of $k_B T_R/d^2$) is universal within at least the XY-like class of models. Near T_R, the facet is circular with radius L given by

$$A\lambda L = 4\sqrt{2}\,k_B T \exp[-\pi^2/4(2|t|\ln 2)^{1/2}], \qquad (8)$$

where $t = (T - T_R)/T_R$. This temperature dependence is radically different from that found by Andreev. [The T dependence of Eq. (8) for van Beijern's model was noted by Cabrera and Garcia[5]]. For $T \to 0$, the facet becomes the expected square. Facet shapes for several representative temperatures are given in Fig. 2. It is easy to show that the right-hand side of Eq. (8) is the step free energy[10] η_0. It is also proportional to the inverse correlation length ξ^{-1} in the low-T phase.[11] Since the step free energy is a surface tension between the two ground states of the model, a standard hyperscaling argument[12] gives $\eta_0 \xi \sim k_B T$, yielding the temperature dependence of the facet size given in Eq. (8).

The shape of the crystal near the facet may be obtained easily in certain special directions. From Ref. 8, the free energy $g(h_x, \eta_y) = \tilde{f}(\vec{\eta}) + h_x\eta_x$ is obtained to order $|h_x|^3$, for $\eta_y = 0$, as

$$g(h_x, 0) = f_0(T) + \eta_0|h_x| + b|h_x|^3, \qquad (9)$$

where $A\eta_0 = k_B T\sqrt{2}\,Z(\omega)$ and b are temperature-dependent constants. A Legendre transformation

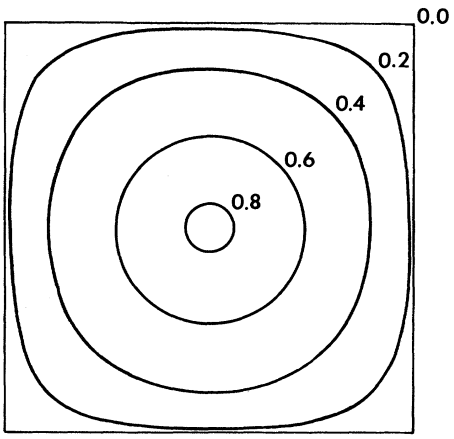

FIG. 2. Facets for the BCSOS model. Temperatures for the facets are indicated in units of T_R, the roughening temperature.

to $\tilde{f}(\eta_x, 0)$ and use of Eq. (3) gives

$$\lambda z(x,0)=\begin{cases} f_0; & |\lambda x|<\eta_0, \\ f_0-\dfrac{2}{3^{3/2}b^{1/2}}(|\lambda x|-\eta_0)^{3/2}; & |\lambda x|\geq\eta_0. \end{cases} \tag{10}$$

This is the (110) direction on the facet and the exponent $\frac{3}{2}$ differs from the mean-field value[2] of 2. In fact, this exponent describes the crystal shape in all directions,[13] and it is universal, reflecting an underlying Pokrovsky-Talapov[14] transition in $\tilde{f}(\vec{\eta})$. Note that the phenomenological treatment of Cabrera and Garcia[5] produces the mean-field exponent.

Consider next a generalized solid-on-solid model described by

$$H=\frac{1}{k_B T}\Big[\sum_{\langle ij\rangle} V(|z_i-z_j|)-ad\sum_i \vec{\eta}\cdot\vec{h}_i\Big], \tag{11}$$

where the z_i are integer-valued heights of atoms at site i, $\langle ij\rangle$ denotes near-neighbor pairs, $\vec{h}_i$ is the lattice gradient of the height at site i, d is the distance between planes, and a is the lattice spacing in the plane. Following Knops,[15] we apply a duality transformation to this Hamiltonian and directly map it onto an XY model at a dual temperature $\tilde{T}=1/T$ in the presence of an (imaginary) applied twist $\vec{\omega}=i(\hat{e}_z\times\hat{\eta})k_B T$. For small $|\vec{\omega}|$ we can compute the free energy $\tilde{f}(\vec{\eta})$ to find[16]

$$\tilde{f}(\vec{\eta})=f_0-\tfrac{1}{2}k_B T K_R|\vec{\eta}/k_B T|^2 d^2, \tag{12}$$

where K_R is the renormalized Kosterlitz-Thouless coupling[17] of the dual XY model. Now Eq. (3) yields the shape of the surface for small $\vec{x}$:

$$\lambda z(\vec{x})=f_0-\tfrac{1}{2}(K_R/k_B T)d^2(\lambda\vec{x})^2. \tag{13}$$

Recall the behavior of K_R in the XY model[6,17]: K_R vanishes for $\tilde{T}>\tilde{T}_c$ and is equal to $2/\pi$ at $\tilde{T}_c$. For $T<T_c$ in the SOS model (which corresponds to $\tilde{T}>\tilde{T}_c$), we have $K_R=0$ and thus from Eq. (13) a facet. The curvature defined earlier has, therefore, the same jump of $2d^2/\pi k_B T_c$ found in the BCSOS model.[18] With the identification in Eq. (13) $\lambda=f_0/z_0$, where f_0 is the free energy per unit area of the flat (001) interface and z_0 is the distance from the center of the crystal to the interface along the (001) direction, we may express the radius of curvature R of the crystal surface by $z_0/R=K_R d^2 f_0/k_B T_c$. Thus at T_c we have the universal jump

$$z_0/R_c=(2/\pi)f_0 d^2/k_B T_c. \tag{14}$$

For the linear dimension L of the facet near T_c, the hyperscaling argument[12] yields $L\propto\xi^{-1}$, where ξ is the correlation length of the dual XY model. The known[17,19] behavior of ξ in the XY model gives $L\sim\exp(-c/\sqrt{t})$ in agreement with the BCSOS model calculation. This universal result is in obvious contrast to mean-field theory.[2]

We point out an important limitation of the SOS-model results for describing equilibrium crystal shapes.[20] The conclusions apply only for facets for which the model is constructed and for surfaces at small angles with respect to it. For large angles they can and do fail. For example, the BCSOS model applies to (100) facets of a bcc crystal but fails near the (110) facet. However, it is easy to construct a BCSOS model for this facet. The free energy $\tilde{f}(-\lambda\vec{x})$ in Eq. (3) must be replaced by $\tilde{f}(-\lambda x, -\lambda y/\sqrt{2})$ yielding elliptical facets near T_R.

The BCSOS construction applies without alteration to the (100) facets of fcc crystals. The six facets of an hcp crystal parallel to the c axis represent the case of the general antiferromagnetic six-vertex model; here the facets are elliptical in shape near T_R and rectangular at $T=0$, and the geometric mean of the principal curvatures undergoes the universal jump $2d^2/\pi k_B T_R$ at $T=T_R$. Details will be given in a forthcoming publication. This hcp case is particularly relevant to ^{4}He crystals, in which roughening transitions have been observed.[21] Curvatures and facet shapes, however, have not yet been carefully studied experimentally.

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