Surface Reconstruction in Crystals

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A model is proposed which shows both a surface-reconstructive phase transition and a faceting transition, depending on the molecular parameters. It involves a further generalization of Lieb's six-vertex problem.

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Recently the problem of the structure of crystal surfaces at a molecular level has been reexamined. Of particular interest has been the Wulff construction[1]; this uses the angle-dependent surface tension of regular crystals to predict the equilibrium shapes of samples which are presumably considerably larger than the correlation length. The idea is to minimize

$$\int dx\,dy\{\tau(\vec{n})[1+(\nabla z)^2]^{1/2}+\lambda z\}, \quad (1)$$

where $z(x,y)$ is the shape of the crystal surface, assumed uniquely defined, with respect to an origin inside the crystal; $\tau(\vec{n})$ is the bulk surface tension for an infinite flat facet with normal $\vec{n}$; and λ is an undetermined multiplier associated with the fixed-volume constraint.

The only exact results known for $\tau(\vec{n})$ were for the planar Ising model[2] and the solid-on-solid model. However, very recently Jayaprakash, Saam, and Teitel[3] have used the Eberlein construction[4] to examine facet formation in a three-dimensional system by suitable restriction of the surface configuration to map the problem onto the six-vertex model.[5] This is analogous to the van Beijeren body-centered solid-on-solid model[6] which has an interesting roughening transition. The calculation of Yang, Yang, and Sutherland[7] which generalizes the original computations of Lieb[8] then yields the angle-dependent surface tension on which the Wulff construction can be carried out explicitly.

In this Letter an alternative approach will be described, which is also exactly solvable in terms of a further generalization of the six-vertex model, and which leads both to a surface-reconstructive phase transition of the type adumbrated by Chui and Weeks[9] and also to a facet-formation transition from a rough state. This approach is based on the terrace-ledge-kink (TLK) model of crystal morphology due to Burton, Cabrera, and Frank[10]; it does not use the Wulff construction directly.

In Fig. 1, the basic geometry of the TLK model is explained. For technical reasons, we work on a lattice rotated at 45°: "straight" ledges then have a zigzag structure. They cannot overlap, nor can they form closed loops but they can touch at vertices of the underlying lattice. Such contacts are counted only once. The configurations map, following Eberlein,[4] onto the six-vertex system illustrated in Fig. 2.

Notice that the number of ledges crossing a 45° line is fixed, being determined by the angle of the crystal face. This suggests a transfer matrix approach at 45° using the Bethe *Ansatz*,[11] which indeed works. The results for the eigenvectors are as follows. For ledges at

$$(x)_n = x_1, \ldots, x_n \text{ with } x_1 < x_{i+1}, \quad 1 \leq x_1,\ x_n \leq 2N, \quad (2)$$

$$\varphi((x)_n) = \sum_p A(p) \prod_1^n \varphi(x \mid k_{p(j)}), \quad (3)$$

where

$$A(p) = (-1)^p \exp[-(i/2) \sum_{i<j} \theta(k_{p(i)}; k_{p(j)})], \quad (4)$$

with

$$e^{i\theta(k,q)} = \frac{w[1+s(k)s(q)]+w^2 s(k)-(e^b-1)s(q)}{w[1+s(k)s(q)]+w^2 s(q)-(e^b-1)s(k)}, \quad (5)$$

and

$$e^{ik} = s(k)[w+s(k)]/[1+ws(k)]. \quad (6)$$

The sum in (3) is over $n!$ permutations of $(1, \ldots, n)$. Finally, the one-particle wave functions

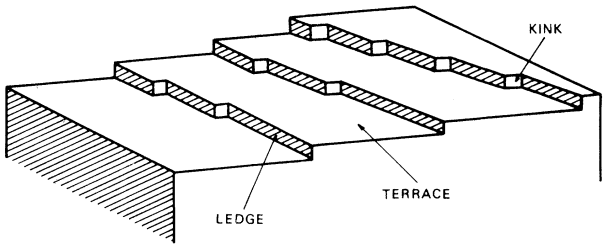

FIG. 1. The terrace-ledge-kink model of a crystal surface. The morphological features referred to in the text are defined pictorially.

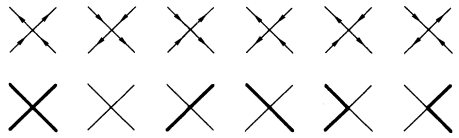

FIG. 2. Six-vertex isomorphism. The first line shows the vertex arrow assignments. In the second, a heavy line corresponds to a positive arrow component in the vertical direction and to a unit height increase stepping from left to right across the line. The third line shows the associated weights. Configurations of ledges are constructed with use of the rule that heavy lines cannot terminate within the lattice.

have the form

$$\varphi(2j\,|k) = a(k)\exp(ikj),$$
$$\varphi(2j-1\,|k) = b(k)\exp[ik(j+\tfrac{1}{2})], \quad (7)$$

with $1 \leq j \leq N$, where

$$s(k) = e^{ik/2}b(k)/a(k). \quad (8)$$

The eigenvalues are given by

$$\Lambda = \prod_1^n \lambda_\pm(k_j), \quad (9)$$

with

$$\lambda_\pm(p) = \{w\cos(p/2) \pm [1 - w^2\sin^2(p/2)]^{1/2}\}^2. \quad (10)$$

The allowed values of the k_j are determined by boundary conditions which are taken to be cyclic rather than open as implied by the model. This should make no difference in the bulk for the thermodynamic limit; thus

$$\exp(ik_jN) = (-1)^n \prod_1^n \exp[i\theta(k_i, k_j)]. \quad (11)$$

Assuming that the Bethe *Ansatz* can be applied and that there are no peculiarities in the thermodynamic limit, we have a density function $\rho(p)$, which would be constant in the free-fermion case $\exp b = 1 - w^2$, given by

$$2\pi\rho(p) = 1 + \int_{-Q}^{Q} \partial_p\theta(p, q)\rho(q)dq, \quad (12)$$

and

$$\tan\theta = \int_{-Q}^{Q} \rho(p)dp, \quad (13)$$

where θ is the angle of slope of the crystal. This system of equations is handled by transforming to the variable s through (6) followed by a bilinear transformation to a difference kernel[12] in (12). The case $\theta = \pi/4$ can be solved explicitly; otherwise, Wiener-Hopf methods are needed.

The salient features of the solution are as follows:

For $b > 0$ (ledge attraction), there is a phase transition at $\exp b = (1+w)^2$. With use of Lieb's ingenious KDP argument,[13] the low-temperature configuration has at least one bound complex of ledges of macroscopic extent. The detailed geometry is not yet available. As Chui and Weeks proposed,[9] this is a natural extension of the surface *binding-unbinding transition.*[14]

The high-temperature phase is presumably rough, but slopes essentially continuously. Once again, it is lamentable that so little is known about the correlation functions here.

For $b < 0$ (ledge repulsion), there is a phase transition of F-model type in the low-temperature phase with a critical w given by $\exp b = (1 - w)$.[2] The high-temperature region includes the free-fermion case, for which the surface can be shown to be rough by studying the ledge pair correlation function. This oscillates with a wavelength $1/\rho$ and decays with an envelope varying as $1/(\text{distance})^2$. The stiffness of the ledges themselves might well be of interest, to know for example whether each one is itself rough or not in the high-temperature phase.

The incremental free energy associated with (12) and (13) is

$$-f^x(b, T, \theta) = (\cos\theta + \sin\theta)\tau_0 + \int_{-Q}^{Q} \rho(q)\ln\lambda_+(q)dq \quad (14)$$

on $0 \leq \theta \leq \pi/4$; here τ_0 is the free energy per unit area of terrace or ledge (assumed equal). It is natural to extend (14) to $\pi/4 \leq \theta \leq \pi/2$ by symmetry. Then in the high-temperature region $f^x(b, \tau, \theta)$ is smooth at $\theta = \pi/4$ whereas it has a cusp in the low-temperature region, like the F-model free energy as a function of polarization.[5,8] This suggests formation of hexagonal prisms.

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