Journal of Statistical Physics, Vol. 34, Nos. 5/6, 1984

Surfaces and Roughening

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Received September 30, 1983

Some recent results in the application of statistical mechanics to surfaces are discussed. Only exactly soluable models are described. First, we consider phase separation below the critical temperature in uniaxial ferromagnets and their analogs. We then consider the determination of the equilibrium shape of a crystal having fixed volume, given the orientation-dependent surface tension, using the Wulff construction.

KEY WORDS: Surfaces; roughening.

1. INTRODUCTION

The aim of this lecture is to describe some recent results in the application of statistical mechanics to surfaces. In view of the restriction of space, only exactly solvable models will be considered, in the hope that, although they neglect many aspects of boundaries in real physical systems, they will nevertheless reveal qualitative truths.

The first problem to be considered is phase separation below the critical temperature in uniaxial ferromagnets and their analogs. This goes back to van der Waals (for fluids),[1] whose theory was subsequently developed by Cahn and Hilliard[2] and by Fish and Widom.[3] All these theories are to a degree phenomenological since they are based on a free energy density functional which is not derived from a Hamiltonian. The

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0022-4715/84/0300-0793$03.50/0

main conclusion is that there is a surface tension and a magnetization profile between oppositely magnetized pure states (or phases) which varies on the scale of the bulk correlation length of a pure phase.[4] On the other hand consider a simple drumhead model in which the interface, or domain wall, is represented by a membrane that has a divergent mean square displacement as the cross-sectional area increases. Such exact results as there are[5,6] favor the latter situation, but the following question is natural: suppose one were able to locate the fluctuating interface. What is the local structure like if such a concept is sensible?

The second problem is the determination of the equilibrium shape of a crystal having fixed volume, given the orientation-dependent surface tension, using the Wulff construction. Until rather recently, the only known results for the surface tension at nonzero temperature were for the planar Ising model; these will be reviewed. In the last few months, some most interesting results have been found for surfaces in three-dimensional systems, based on the Eberlein construction.[7] One line of approach is via the aforementioned Wulff plot, and the other is essentially through the terrace–ledge–kink (TLK) model of Burton, Cabrera, and Frank.[8] In this way, examples of phase transitions with facet formation and associated deroughening can be found, as well as examples of surface reconstruction.

2. PHASE SEPARATION IN THE PLANAR ISING MODEL

Consider the geometry and parametrization shown in Fig. 1. Let the magnetization at the point (x, y) be $m(x, y \mid N)$. The following limiting

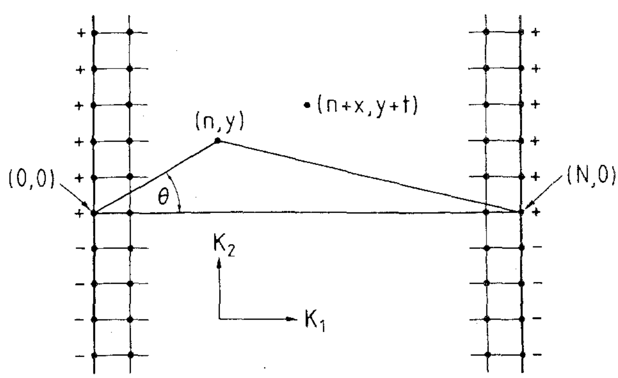

Fig. 1. Ising strip lattice showing coordinates, boundary conditions, and labeling of nearest-neighbor ferromagnetic couplings in units of $k_B T$.

result can be obtained[5]: $\beta \in (-1, 1)$,

$$\lim_{N\to\infty} m\big((1+\beta)N/2, \alpha N^{1/2} \mid N\big) = m^* \operatorname{sgn} \alpha \Phi\left[\frac{b|\alpha|}{(1-\beta^2)^{1/2}}\right] \tag{1}$$

where m^* is the spontaneous magnetization,[9] $b = [\sinh 2(K_1^* - K_2)]^{1/2}$ with $\exp 2K^* = \coth K$ and

$$\Phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2}\, du \tag{2}$$

The surface tension associated with the phase transition is defined as

$$\tau(0) = \lim_{N\to\infty} \frac{1}{N} \log(Z^+/Z^{+-}) \tag{3}$$

where the argument of the logarithm is the ratio of partition functions for infinite strips, Z^{+-} for boundary conditions as in Fig. 1, but Z^+ having + spins on the boundary and therefore no separation of phase. A calculation shows that

$$\tau(0) = 2K - \log\coth K \tag{4}$$

Fisher, Fisher, and Weeks[10] made an extremely useful observation about (1): the limiting result can be obtained heuristically from simple fluctuation theory, provided an angle-dependent surface tension is used[6]; this is obtained by sliding up the right-hand edge of the strip in Fig. 1. The simplest, and completely rigorous, calculation is to use duality to a pair correlation function between boundary spins with free edges.[11] The only further assumption needed to recapture (1) is that on crossing the interface the state changes abruptly between homogeneous phases; this surely cannot be precisely true, and indeed is not, as will now be shown.

Define

$$\tilde{m}(x, y) = \lim_{N\to\infty} m(x, y \mid N) \tag{5}$$

Then an intrinsic magnetization $m_{\text{int}}(y \mid n)$ will be defined by

$$\partial_y m_{\text{int}}(n, y) = \sum_{y_0} P_{\text{cap}}(y_0 \mid n)\, \partial_y m_{\text{int}}(y - y_0 \mid n) \tag{6}$$

through a suitable choice of $P_{\text{cap}}(y_0 \mid n)$ motivated by fluctuation theory alluded to above. The operation ∂_y is a partial difference inserted for analytical convenience. The idea of the convolution structure in (6) is to remove the capillary fluctuations from $\tilde{m}$ to get m_{int}. The motivation is Ornstein–Zernike theory. Recently $\tilde{m}(n, y)$ has been calculated exactly for large n and (6) has been solved by Fourier methods to give $m_{\text{int}}(y \mid \infty)$ as an integral:

$$m_{\mathrm{int}}(y \mid \infty) = \frac{m^*}{2\pi} \int_0^{2\pi} d\omega\, e^{iy\omega} g(\omega)/(e^{i\omega} - 1) \tag{7}$$

where

$$g(\omega) = \frac{1}{1 + e^{i\delta^*(\omega)}} \left(\frac{B}{A} \right)^{1/2} \left[\left(\frac{e^{i\omega} - A}{e^{i\omega} - B} \right)^{1/2} \left(\frac{1 - B^{-1}}{1 - A^{-1}} \right)^{1/2} + \left(\frac{e^{i\omega} - B^{-1}}{e^{i\omega} - A^{-1}} \right)^{1/2} \left(\frac{1 - A}{1 - B} \right)^{1/2} \right] \tag{8}$$

with

$$e^{i\delta^*(\omega)} = \left(\frac{B}{A} \right)^{1/2} \left[\frac{(e^{i\omega} - A)(e^{i\omega} - B^{-1})}{(e^{i\omega} - A^{-1})(e^{i\omega} - B)} \right] \tag{9}$$

where $A = \coth K_1^* \coth K_2$, $B = \coth K_1^* \tanh K_2$.

The pair correlation can also be conditioned by the device of (6) so that one point lies a given distance, say y, from the interface. Suppose the other has a relative coordinate $(x, 0)$; (see Fig. 1) then the conditioned function $C(x \mid y)$ is given by

$$C(x \mid y) \sim m_{\mathrm{int}}(y) \frac{1}{2\pi} \int_0^{2\pi} e^{-x[\gamma(\omega) - \gamma(0)]}\, d\omega \tag{10}$$

where

$$\cosh \gamma(\omega) = \cosh 2K_1^* \cosh 2K_2 - \sinh 2K_1^* \sinh 2K_2 \cos \omega \tag{11}$$

as $x \to \infty$, which behaves as $1/\sqrt{x}$ in this regime. This proves the existence of long-ranged correlations in the interface, as suggested by Wertheim[12] and Weeks.[13]

3. PHASE TRANSITIONS IN SURFACES

Returning to the notion of an orientation-dependent surface tension and the Wulff construction, the equilibrium shape of a crystal denoted S is given by[14]

$$\min_S \left[\int \tau(\mathbf{n}_s)\, dS + \lambda V(S) \right] \tag{12}$$

where S labels the surface with normal $\mathbf{n}_s$, included volume $V(S)$, and a Lagrange multiplier λ. The surface tension $\tau(\theta)$ for the planar Ising model as a function of angle θ is known, giving the plots of Figs. 2a and 2b. There are cusps at $T = 0$ corresponding to facets which roughen for $T > 0$ giving a smooth mean shape about which there are large fluctuations.

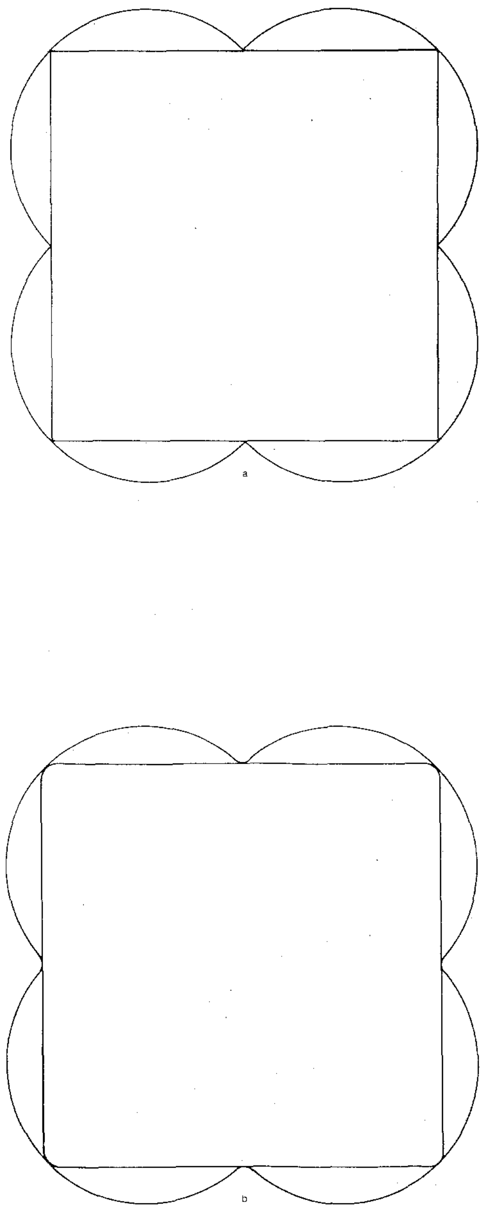

Fig. 2. The Wulff construction. In each case the outer curve is a polar plot of the surface tension. The inner is the crystal shape (up to a scale factor) determined as follows: for each angle θ draw a line L_θ from the origin to cross the surface tension curve. At the intercept draw a perpendicular to L_θ. The inner envelope of all perpendiculars is the crystal shape. For (a), $k_B T/J = 0$, whereas for (b), $k_B T/J = 0.1$.

The orientation-dependent surface tension for the BCSOS model[15] has recently been obtained.[16] This model is based on the Eberlein construction[7] of a surface associated with a square lattice: crossing each edge of the lattice the height of the surface changes by exactly ± 1. This is labeled by a directed arrow on the edge. Height conservation round closed loops is *guaranteed* by the six-vertex construction[7] (see Fig. 3). Van Beijeren showed that such a model has a phase transition of Rys-F type[17] from a flat low-temperature structure with bounded height fluctuation to a rough high-temperature structure with

$$\langle (h|0) - [h(r)]^2 \rangle \sim A(T)\log|r| \tag{13}$$

where $h(x)$ is the height at point x. To carry out the Wulff construction, one needs the vertex weight assignments with nonzero η_i; this case was solved by Sutherland, Yang, and Yang.[17] It turns out that the crystal shape is determined completely by the free energy as a function of horizontal and vertical electrical fields.

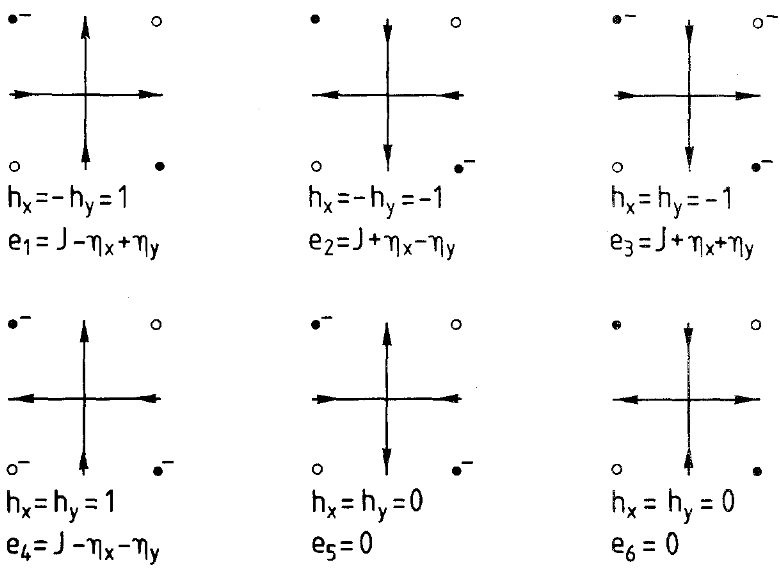

Fig. 3. Wulff construction for the BCSOS model on the (100) face. The filled circles represent atoms in the top layer of the lattice, whereas the open circles represent atoms a half-layer down at the body-centered positions. A minus sign indicates that the top atom is missing. Only in-plane bond energies with value $-J$ appear. The variables h_i for $i = x, y$ are the height differences in the coordinate directions, corresponding to polarizations in the usual six-vertex notation. The h_i are coupled to electric field variables η_i, $i = x, y$.

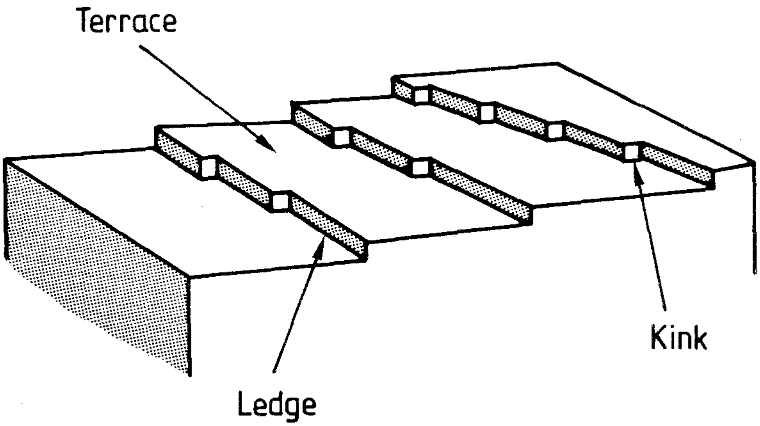

Fig. 4. Morphology of the terrace–ledge–kink (TLK) model. The terraces have neither pits nor adatoms.

A brief summary of the conclusions is as follows:

1. There is a phase transition at the F-model transition $T_R(J) = J/k_b \log 2$.

2. For $T > T_R(J)$, the surface is approximately spherical and as $T \to T_R(J)+$ the curvature goes to a finite limit.

3. When $T \to T_R(J)-$, the curvature jumps to zero over a facet of radius R given by

$$\lambda R \sim \text{const} \exp\left\{ -\text{const}/\left[T_R(J) - T \right]^{1/2} \right\} \tag{14}$$

where Λ is the Lagrange multiplier which fixes the volume. The facet goes over to a square as $T \to 0$.

There is another Eberlein construction which is associated with the terrace–ledge–kink (TLK) model of Burton, Cabrera, and Frank,[8] illustrated in Fig. 4. For technical reasons, a lattice rotated at 45° is used; straight ledges correspond to zig-zag structures; they which cannot overlap or form closed loops but they can touch at vertices of the underlying lattice. Such contacts are counted only once. The vertex weights are shown in Fig. 5. The statistical mechanical problem is to solve the six-vertex problem with horizontal and vertical fields, but with the simultaneous restriction that the number of ledges be fixed. This is a generalization of Sutherland, Yang, and Yang[17] which fortunately can be solved exactly. The main results are as follows:

1. When $b > 0$ (ledge attraction), there is a phase transition at $e^b = (1 + w)^2$ to a low-temperature phase in which the ledges aggregate into

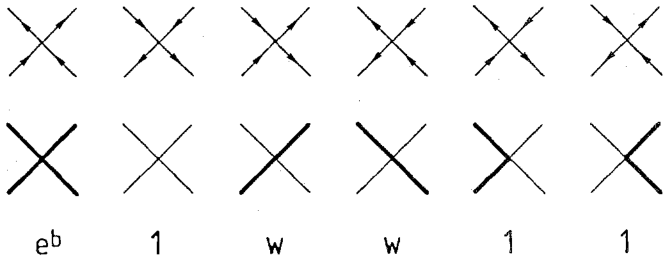

Fig. 5. Vertex configurations for the six-vertex version of the TLK model. From the right, the vertices 6 and 5 correspond to straight ledges. Vertices 4 and 3 are kinks with Boltzman weight $w \leqslant 1$. Vertex 2 is a terrace site. Vertex 1, with weight e^b, is a meeting of two ledges.

a finite number of macroscopic cliffs. The high-temperature phase is rough with a uniform distribution of ledges. The ledge–ledge correlation function oscillates with a period or (1/density of ledges) and a power-law envelope which gives a rough surface.

2. When $b < 0$, there is a phase transition only when the angle of surface is $\pi/4$, which presumably involves facet formation, with an *octagonal* crystal structure.

There is also an interesting paper by Blöte and Hilhorst[(18)] in which a roughening transition is associated with the zero-temperature triangular Ising model. This appers to be of the TLK-reconstructive rather than of the BCSOS type.

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