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Exact equilibrium crystal shapes at nonzero temperature in two dimensions

Craig Rottman and Michael Wortis
Department of Physics and Material Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801
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We calculate for the two-dimensional Ising model at arbitrary temperature T the exact equilibrium shape of a large "crystal" of one phase (up) embedded in the other (down). Low-temperature properties of the interfacial free energy for an interface of arbitrary orientation are also discussed.

I. INTRODUCTION

When two phases coexist at temperature T, a large inclusion of one can exist at equilibrium in the other. The equilibrium shape of such an inclusion is determined by minimizing the total interfacial free energy at fixed included volume. For isotropic phases (e.g., fluids) this leads to a spherical equilibrium shape; however, when (as in crystals) the interfacial free-energy density $f_i(\hat{n},T)$ depends on orientation $\hat{n}$ with respect to a set of reference directions (local crystal axes), the shape of the inclusion will adjust to take advantage of low (free-energy)-cost interfaces and avoid high-cost interfaces, resulting in a "crystal" shape which is not spherical and, indeed, changes with temperature.

If the interfacial free-energy density $f_i(\hat{n},T)$ is known for all orientations $\hat{n}$, then the Wulff construction[1-3] determines the equilibrium shape of a large crystal.[4] Previously, equilibrium shapes have been determined only at $T=0$, where f_i can easily be determined for arbitrary $\hat{n}$ (Refs. 2 and 5); however, interfacial free energies are not generally available for arbitrary orientation at $T>0$. It was pointed out recently that, for the $d=2$ nearest-neighbor (NN) Ising model on the square lattice, $f_i(\hat{n},T)\equiv f_i(\theta,T)$ is related by duality to the spin-spin correlations in the high-temperature region.[6] Since the large-distance behavior of these correlations is known,[7] it is possible to carry out the Wulff construction at all temperatures.

It is the purpose of this paper to investigate, as a function of T, the exact equilibrium shapes which result. Flat faces and sharp corners are present[8] at $T=0$. Because the roughening temperature $T_R=0$ in two dimensions, we find for all θ and all $T>0$ a continuously curved equilibrium shape, with no flat faces or sharp corners. As $T\to T_c^-$, this shape becomes spherical. We are aware of no previous exact calculations of crystal shapes at nonzero temperature. We also discuss analytically the mechanism by which the continuously curved shape evolves from the faceted shape as T increases from zero.

II. RESULTS

The interfacial free energy per unit length $f_i(\theta,T)$ of the $d=2$ NN Ising model is related to the two-point correlation function of the dual $d=2$ Ising model by the following equation[6]:

$$f_i(\theta,T)=-k_BT\lim_{L\to\infty}\left[\frac{1}{L}\ln\langle\sigma_{00}\sigma_{MN}\rangle\right]. \quad (1)$$

Here $L=(M^2+N^2)^{1/2}$ and θ is defined such that $M=L\,|\cos\theta|$ and $N=L\,|\sin\theta|$ as $L\to\infty$. The high-temperature correlation function $\langle\sigma_{00}\sigma_{MN}\rangle$ of Eq. (1), which is known for $T^*>T_c$ for large M and N,[7] depends implicitly on the temperature $T<T_c$ via the duality relation $e^{-2K}=\tanh K^*$, where $K^*=J/k_BT^*$, $K=J/k_BT$, and J is the NN coupling.[9] We find

$$\beta f_i(\theta,T)=|\cos\theta|\sinh^{-1}(\alpha|\cos\theta|)+|\sin\theta|\sinh^{-1}(\alpha|\sin\theta|),$$
$$\alpha=\frac{2}{b}\left[\frac{1-b^2}{1+(\sin^2 2\theta+b^2\cos^2 2\theta)^{1/2}}\right]^{1/2}, \quad (2)$$
$$b=\frac{2\sinh 2K}{\cosh^2 2K},\quad \beta=(k_BT)^{-1}.$$

For special angles Eq. (2) reduces to the following well-known expressions[10,11]:

$$\beta f_i(\theta=0,T)=2K+\ln(\tanh K), \quad (3a)$$
$$\beta f_i(\theta=\pi/4,T)=\sqrt{2}\ln(\sinh 2K). \quad (3b)$$

The equilibrium shape $R(\phi,T)$ can be found parametrically[12]:

$$R = R_0(x^2+y^2)^{1/2} ,$$
$$x = (\cos\theta) f_i - (\sin\theta)\frac{df_i}{d\theta} , \tag{4}$$
$$y = (\sin\theta) f_i + (\cos\theta)\frac{df_i}{d\theta} ,$$
$$\tan\phi = y/x .$$

Figures 1–4 exhibit polar plots of $f_i(\theta,T)$ and $R(\phi,T)$ for several reduced temperatures k_BT/J. The Wulff construction,[1–3] leading from $f_i(\theta)$ to $R(\phi)$, is illustrated in Fig. 3: Through each point on the curve $f_i(\theta)$ draw a line perpendicular to the radius joining that point to the center. The interior envelope of these lines is $R(\phi)$. For $T=0$ (Fig. 1), $f_i(\theta)$ is cusped and the point of each cusp determines an entire crystal face. Lines through the remaining points of $f_i(\theta)$ all intersect at the crystal corner, which is sharp. The cusp is absent[13] at $T>0$ (Figs. 2–4) because all interfaces are rough, so the interior envelope becomes continuously curved. For low enough temperatures (Figs. 2 and 3), the crystal is only slightly rounded. As $T\to T_c^-$, $f_i(\theta)$ becomes isotropic and the crys-

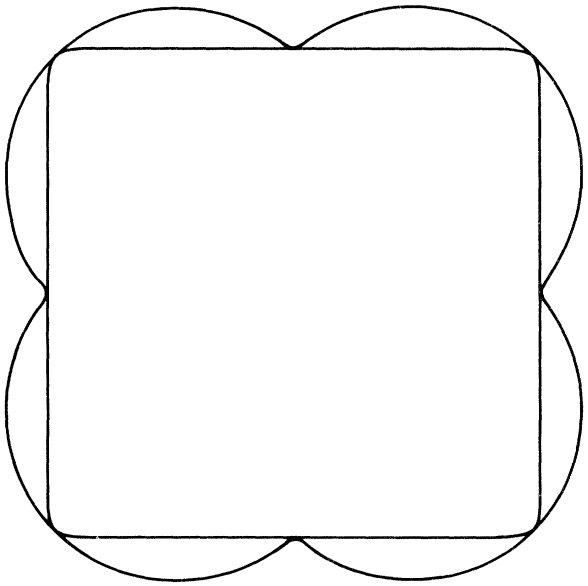

FIG. 2. Interfacial free-energy density $f_i(\theta,T)$ (outer line) and equilibrium crystal shape $R(\phi,T)$ (inner line) for $k_BT/J=0.1$.

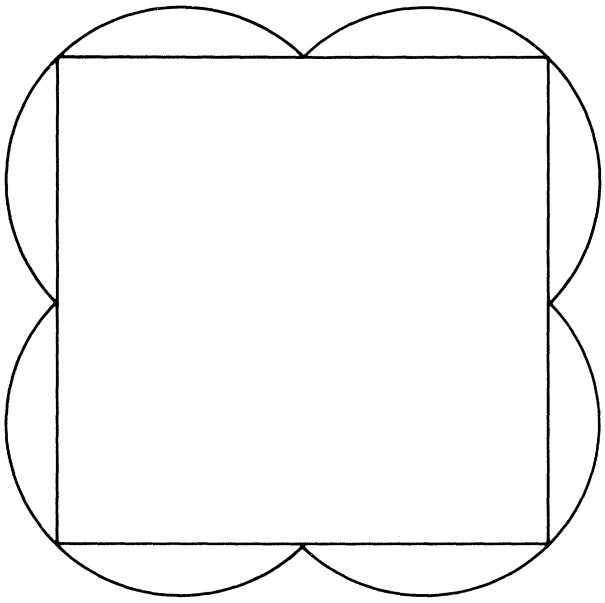

FIG. 1. Interfacial free-energy density $f_i(\theta,T)$ (outer line) and equilibrium crystal shape $R(\phi,T)$ (inner line) for $k_BT/J=0$.

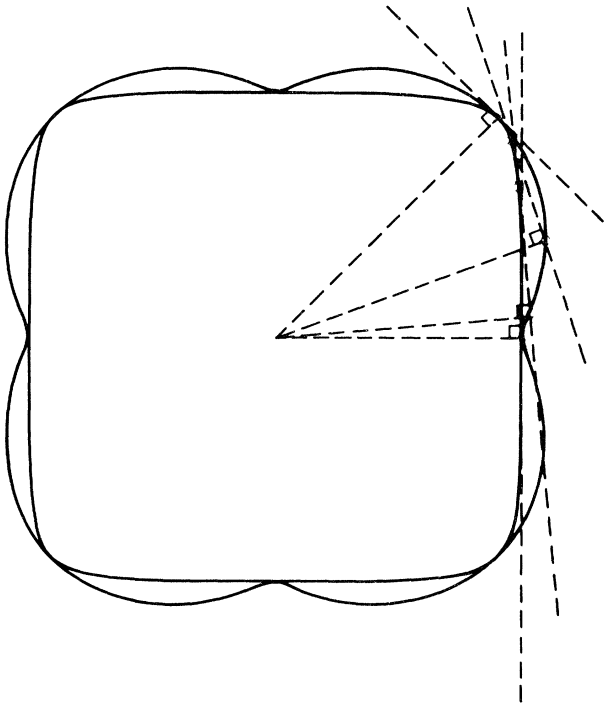

FIG. 3. Interfacial free-energy density $f_i(\theta,T)$ (outer line) and equilibrium crystal shape $R(\phi,T)$ (inner line) for $k_BT/J=0.3$. The Wulff construction (see text) is indicated at several representative points on $f_i(\theta)$.

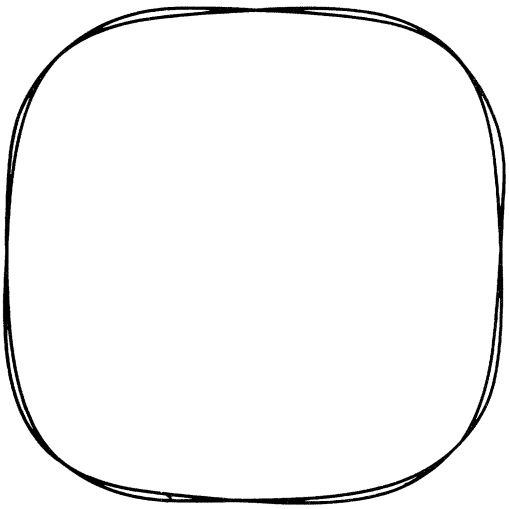

FIG. 4. Interfacial free-energy density $f_i(\theta,T)$ (outer line) and equilibrium crystal shape $R(\phi,T)$ (inner line) for $k_BT/J=0.6$.

tal shape is circular. Recall that $k_BT_c/J=2/\ln(1+\sqrt{2})\simeq 2.269$. It is striking (Fig. 4) that already at a reduced temperature $T/T_c<\frac{1}{2}$, the crystal shape is almost circular. This reflects the fact that the $d=2$ correlations (of the dual model) are nearly isotropic well above T_c.

The expression for $f_i(\theta,T)$, and in turn, properties of the crystal shape, can be expanded for low temperatures and/or near special angles. For instance, the expansion of f_i when θ and $z=e^{-2K}$ are both of order ϵ ($\epsilon<<1$) displays the nonanalyticity of f_i at $\theta=z=0$:

$$\beta f_i=2K-(\theta^2+4z^2)^{1/2}+|\theta|\sinh^{-1}(|\theta|/2z)+O(\epsilon^2\ln\epsilon)\ . \tag{5}$$

Similarly the crystal shape can be characterized near $\phi=0$ by

$$x\sim 1-[Ke^{-2K}+O((e^{-2K})^2)]y^2+O(y^4)\ , \tag{6}$$

and near $\phi=\pi/4$ by

$$x+y\sim 1-[K+O(1)](x-y)^2+O((x-y)^2)\ . \tag{7}$$

For low temperatures we find, from Eq. (2),

$$f_i=2J(|\cos\theta|+|\sin\theta|)+k_BT[|\cos\theta|\ln|\cos\theta|+|\sin\theta|\ln|\sin\theta| -(|\cos\theta|+|\sin\theta|)\ln(|\cos\theta|+|\sin\theta|)] -k_BT\frac{|\cos\theta|^3+|\sin\theta|^3}{|\cos\theta|\,|\sin\theta|}e^{-4K}+O(e^{-8K})\ . \tag{8}$$

Each term in Eq. (8) can also be independently obtained from a low-temperature expansion as follows: Consider interfaces with one end fixed at the origin and the other end fixed at (M,N). The interfacial energies associated with the broken bonds of the interfaces are

$$E_n=2J(M+N)+4nJ,\quad n=0,1,2,\ldots\ . \tag{9}$$

Construct the partition function

$$Z=g(E_0)e^{-\beta E_0}+g(E_1)e^{-\beta E_1}+\cdots=e^{-\beta E_0}g(E_0)\left[1+\frac{g(E_1)}{g(E_0)}e^{-\beta(E_1-E_0)}+\cdots\right]\ . \tag{10}$$

The degeneracies $g(E_n)$ can be obtained from simple combinatorial analysis[14]:

$$g(E_0)=\binom{M+N}{M},\quad g(E_1)=\binom{M+N}{M-1}(M-1)+\binom{M+N}{N-1}(N-1),\ldots\ . \tag{11}$$

Using Stirling's formula and substituting $M=L\,|\cos\theta|$ and $N=L\,|\sin\theta|$, Eq. (8) is obtained.

Two interesting aspects of this expansion should be noted. First, we are expanding about an infinitely degenerate ground state. The expansion is easy to perform because the model is two dimensional, so that all degeneracies are easily calculable. Second, Eq. (8) diverges term by term at $\theta=0$. This is related to the roughening transition at $T=\theta=0$. To obtain Eq. (3a) an appropriate resummation must be performed. For $\theta\neq 0$, the series is well behaved, since at $T=0$ the interface is already rough (i.e., no phase transition takes place for $0\leq T<T_c$).

Last, we discuss the solid-on-solid (SOS) model in $d=2$ and its relationship to the above Ising-model results. The interfacial free energy per unit length is[5,15]

$$\beta f_i^{\mathrm{SOS}}(\theta,T)=\eta\,|\sin\theta|+\left[2K+\ln\left[\frac{\cosh 2K-\cosh\eta}{\sinh 2K}\right]\right]|\cos\theta|\ , \tag{2'}$$

$$\eta=\ln\{[(\cos^2\theta+\sin^2\theta\sinh^2 2K)^{1/2}+|\sin\theta|\cosh 2K]/(|\sin\theta|+|\cos\theta|)\}\ .$$

For $\theta=0$, it turns out that Eq. (2') reduces to Eq. (3a). The Ising-model crystal shape is similar to the crystal shape derived from Eq. (2') for low temperatures and small angles, as expected; in fact, Eqs. (5) and (6) apply, to the orders indicated, for the SOS as well as the Ising model. However, the low-temperature expansion becomes

$$f_i^{\mathrm{SOS}}=2J(|\cos\theta|+|\sin\theta|)+k_BT[|\cos\theta|\ln|\cos\theta|+|\sin\theta|\ln|\sin\theta| -(|\cos\theta|+|\sin\theta|)\ln(|\cos\theta|+|\sin\theta|)]$$

$$-k_BT\frac{|\cos\theta|^3}{|\sin\theta|}e^{-4K}+O(e^{-8K})\ , \tag{8'}$$

and therefore f_i^{SOS} does not have fourfold rotational symmetry [$f_i^{\mathrm{SOS}}(\theta)\neq f_i^{\mathrm{SOS}}(\theta+\pi/2)$].

Note added in proof. Avron and co-workers[16] have recently communicated similar calculations for the case $J_x\neq J_y$.

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