Total surface energy and equilibrium shapes: Exact results for the $d=2$ Ising crystal

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Explicit relations between the surface tension (interfacial energy density), the equilibrium shape of a crystal, and the total surface energy are given. For the $d=2$ Ising model with anisotropic couplings, the exact equilibrium shape is cast into a closed form of elementary functions. The surface energy is compared with Monte Carlo simulations. A discussion of the solid-on-solid approximation is presented.

A very old problem—the shape of a crystal (or droplet) in equilibrium with the vapor—has recently received considerable attention. Part of this revived interest is due to the connections between the equilibrium shape (ES), the surface tension[1] (ST), and the roughening transition.[2,3]

If the ST is independent of the orientation of the surface, it is an elementary exercise in the calculus of variations to obtain the ES which (in any dimension) is a sphere. For crystals, where the ST depends on orientation, the problem is less mundane. In particular, in these cases, the interesting possibility of a roughening transition exists.

Given an orientation-dependent ST, the problem of constructing the ES was solved nearly a century ago.[4] However, calculating the ST (within the framework of statistical mechanics) is an extremely hard problem and at present only for the $d=2$ Ising model is this problem solved. Specifically, the asymptotic behavior of a general two-spin correlation function, for large separation was calculated explicitly by Cheng and Wu in 1967.[5] That σ, the ST, may be obtained by duality from this asymptotic behavior was possibly known[6] by 1963 and has been rediscovered many times since.[7] These facts have all been put together recently to give the ES of the $d=2$ Ising model.[8,9] Both are short of a number of interesting results which we wish to report here. First, some general results relating the ES and the ST in arbitrary d are presented. Then, specializing to the $d=2$ Ising case, we give the exact ES in a closed form of elementary functions. We also describe formulas for the total surface free energy, internal energy, the curvatures of the ES and scaling properties. Finally, we make some comments on the solid-on-solid approximation to the ST and the ES.

Let $\sigma(\hat{n})$ denote the ST of a planar interface with normal[10] $\hat{n}$ and $R(\hat{r})$ the radius of the ES in the direction of $\hat{r}$. Wulff's theorem may be stated analytically as

$$\lambda R(\hat{r})=\min_{\hat{n}}\sigma(\hat{n})/(\hat{n}\cdot\hat{r}), \tag{1}$$

where λ is just a scale adjusted to yield the volume of crystal. In regions where $\sigma(\hat{n})$ is differentiable, the (local) minimum is the solution to $\nabla_i(\ln\sigma) = \tau_{ik}r_k/(\hat{n}\cdot\hat{r})$ where $\tau_{ik}\equiv\delta_{ik}-n_in_k$ is the transverse projector and[11] $\nabla_i\equiv\tau_{ik}\partial_k$. Since it is the global minimum which enters into (1) some care must be exercised in using the last formula. With that proviso, $\vec{R}\equiv R\hat{r}$ is given by[12,13]

$$\lambda\vec{R}=\hat{n}\sigma+\vec{\nabla}\sigma. \tag{2}$$

It follows that if the ST is stationary at $\hat{n}$ then $\lambda\vec{R}=\sigma\hat{n}$ and $\hat{n}=\hat{r}$. For completeness we state a "converse" of formula (2): $\lambda\hat{n}/\sigma=\hat{r}/R+\vec{D}(1/R)$ where $\vec{D}$ are the transverse derivatives with respect to $\hat{r}$. Note that σ determines a unique R but the converse is false in general. In general, $\vec{\nabla}\sigma$ may be discontinuous (kinks in σ) and, associated with the direction in which these kinks occur, the ES can develop facets. In $d=2$, a facet is a straight line, whose length is bounded (from above) by the value of the discontinuity.[14]

One useful consequence of Wulff's construction is a simple formula for the total surface energy Σ of an equilibrium crystal with volume V. Let W be the volume bounded by $R(\hat{r})$ as given by (1) with $\lambda=1$.

Then

$$\Sigma = dW^{1/d}V^{1-1/d}. \tag{3}$$

Only the factor d may be a surprise, the others are expected on dimensional and scaling grounds alone. This quantity is of interest in some Monte Carlo studies (see below).

Another consequence is the relationship between an ES which has been scaled *anisotropically* and its coresponding ST: $\tilde{\sigma}$. Consider the anisotropic scaling operation S on a vector: $(S\vec{A})_i = \mu_i A_i$ (no sum) where μ_i are arbitrary (positive) constants. Let I denote the inversion operation: $I\vec{A} = \hat{A}/|\vec{A}|$. Consider $\tilde{\sigma} \equiv ISI(\sigma\hat{n})$. The ES constructed from $\tilde{\sigma}$ is $S^{-1}\vec{R}$. Thus, if σ were an "inverted ellipse," the ES will be an ellipse. This turns out to be the case for the Ising model near T_c.

The curvature at any point on the ES is related to the matrix $\nabla_i R_j = (\tau_{ij}\sigma + \tau_{ik}\tau_{jl}\partial_k\partial_l\sigma)/\lambda$. Note that $n_i\nabla_i R_j = 0$ so that it is a linear (self-adjoint) operator on the tangent plane. The other $d-1$ eigenvalues of $\nabla_i R_j$ are the principal radii of curvature. In $d=2$, the only radius of curvature is therefore the trace of this matrix.

Finally, we remind the reader of one definition of a roughening transition[2]: The vanishing of some kink in σ as T approaches the transition temperature from below. Since a facet in the ES implies a kink in the ST, the vanishing of a facet is a signature for a roughening transition. However, experimentally, it may be quite difficult to determine unambiguously whether a facet is flat or one with very low curvature. Indeed, in two dimensions all interfaces are rough for $T > 0$ but are flat looking for small T.

For the remainder of this Communication we specialize to the $d=2$ Ising model where the exact ST and ES may be obtained. A convenient parametrization of $\hat{n}$ is ϕ, where $\cos\phi \equiv \hat{n}\cdot\hat{x}$. The ST will be denoted by $\sigma(\phi)$ and $\dot{\sigma} \equiv \partial\sigma/\partial\phi$.

For the Ising model with nearest-neighbor anisotropic couplings ($J_x \neq J_y$), on a square lattice, $\sigma(\phi)$ may be extracted[6–9] from the results in Ref. 5. The explicit form[9] is not very transparent. It is far better to start from the defining relations[5] for the functions α_x and α_y

$$\begin{aligned} &h_x\cosh\alpha_x + h_y\cosh\alpha_y = 1, \\ &h_y\sinh\alpha_y = (\tan\phi)\, h_x\sinh\alpha_x, \end{aligned} \tag{4}$$

where

$$\begin{aligned} &h_x = \tanh 2\beta J_y/\cosh 2\beta J_x, \\ &h_y = \tanh 2\beta J_x/\cosh 2\beta J_y. \end{aligned} \tag{5}$$

These α's enter into the formula for σ via

$$\beta\sigma(\phi) = \alpha_x\cos\phi + \alpha_y\sin\phi, \tag{6}$$

where $\beta \equiv 1/kT$. It is easy to check that, except at $T=0$, σ has no kinks and that the two-dimensional version of (2) applies. The result for the equilibrium shape is remarkably simple ($\tilde{\beta} \equiv \beta\lambda$) :

$$x \equiv R_x = \alpha_x/\tilde{\beta}, \quad y \equiv R_y = \alpha_y/\tilde{\beta}. \tag{7}$$

Now we can, using (4), dispense with the parameter ϕ completely and write a closed form

$$h_x\cosh(\tilde{\beta}x) + h_y\cosh(\tilde{\beta}y) = 1. \tag{8}$$

In the isotropic case ($J_x = J_y = J$), (4) and (7) reduce further to

$$\cosh\xi\cosh\eta = \tfrac{1}{2}\cosh 2\beta J\coth 2\beta J, \tag{9}$$

where ξ, η are the rotated coordinates $\tilde{\beta}(x \pm y)/2$.

Near $T=0$, the shape is practically a rectangle with J_x/J_y being the ratio of the sides. To see how "flat" the sides are, we compute the radius of curvature $\rho(\phi)$ at $\phi=0$ and $\pi/2$. At these points $\lambda R = \sigma$ so that $\rho/R = 1 + \ddot{\sigma}/\sigma$ which is $\dot{y}/x$ and $-\dot{x}/y$, respectively. The result at $\phi=0$, e.g., is

$$\rho/R = (\sinh A)/A \underset{T\to 0}{\longrightarrow} e^{2\beta J_x}/4\beta J_x, \tag{10}$$

where $A = \cosh^{-1}[(1-h_y)/h_x]$. For the equal couplings case, this is identical to those in Ref. 8. From the graphs[8,9] of the ES, it is clear that for T well above zero, the roughening temperature, the faces look flat. The exponential growth of the radius of curvature ($\cosh\beta \to \infty$) reflects the exponential growth[9] of $\ddot{\sigma}$ which shows how a kink develops as $T \to 0$.

One could also ask how the radii of curvature vanish at the "corner," i.e., where the maximum of $R(\phi)$ occurs. The result is $\rho/R \propto T$ as $T \to 0$. The proportionality constant for general couplings is the solution to a transcendental equation which does not display any properties of interest to us. For the equal coupling case, it is simply $k/2J$, as obtained in Ref. 8 also.

For $T \to T_c$, $\sigma(\phi)$ vanishes everywhere since $h_x + h_y = 1$ at T_c. One can check the well-known fact that σ is proportional to $T_c - T$ and that it is an "inverted ellipse." Thus, the ES, near T_c, is an ellipse with the ratio of the axes being $\sinh 2\beta_c J_x$ ($= 1/\sinh 2\beta_c J_y$), where $\beta_c = 1/kT_c$. For the equal coupling case, the shape becomes a circle which is related to the isotropy at the scaling limit. An easy way to see the ellipse and associate features is to expand the cosh in (8) for small arguments, leading to $h_x x^2 + h_y y^2 = 2(1 - h_x - h_y)/\tilde{\beta}^2$. Equation (8) also allows us to conclude that, except at $T=0$ and near T_c, no (temperature-dependent) rescaling of x and y can bring the general ES into the equal coupling case. The ES is an *intrinsic property of the couplings* and not related simply to unequal lattice spacings in the two directions.

Since σ is a kind of "free" energy associated with interfaces, we interpret Σ as the free surface energy. Defining $E \equiv \partial(\beta\Sigma)/\partial\beta$, we would interpret it as the average energy of the droplets. As $T \to 0$, both Σ and E approach $8\sqrt{J_x J_y V}$. But near T_c, although Σ vanishes, E approaches a finite limit. This is a special feature of the two-dimensional Ising model, where $\Sigma \propto T_c - T$. This finite value is $(16\pi V \sinh 2\beta_c J_y)^{1/2} \times [J_x + J_y(\sinh 2\beta_c J_x)]$, which reduces to $8J\sqrt{\pi V}$ in the equal coupling case. For arbitrary T, we are unable to integrate (8) into a close form. However, $\beta\Sigma E/V$ is just $2\partial(\beta^2 W)/\partial\beta$ which is integrable. We quote the equal coupling case ($h_x = h_y = h$)

$$\frac{\beta\Sigma E}{V} = 32J\left(\frac{1-6\epsilon+\epsilon^2}{1-\epsilon^2}\right)K(m), \tag{11}$$

where $\epsilon \equiv \exp(-4\beta J)$, $m \equiv 1-4h^2$, $h = h_x = h_y$, and $K(m)$ is the elliptic integral of the first kind.[15] The general case, involving the second and third elliptic integrals, is quite complicated. Unable to see any interesting features, we do not quote it here.

In Monte Carlo studies[16] of droplets, it is easy to find E: Count the broken bonds which make up the boundary of the droplets of a certain size (l is the number of minus spins in a sea of pluses, for example) and average this quantity (for fixed l). Since the configurations are generated according to their Boltzmann weights, such an average is readily obtained (by contrast the ES is far more difficult to extract from a Monte Carlo study). For the equal coupling case and $2\beta J = 2$ and 1.5, $E/(8J\sqrt{l})$ is found[17] to lie in the range [1.18,1.21] and [1.33,1.38], respectively. These results compare with 1.21 and 1.34 which we computed by numerical integration (for W) and Eq. (11).

Before concluding, we make some remarks concerning the solid-on-solid (SOS) approximation[18] for σ. It was explicitly given by Burton, Cabrera, and Frank[19] in the equal coupling case. The anisotropic result is a trivial generalization[9] which shows how differently J_x and J_y enter. Even in the latter case, this approximation is exact for all $T \leq T_c$ if $\phi = 0, \pm\pi/2, \pi$. This miracle is a consequence of delicate cancellations between overhang contributions and interactions between the interface and bubbles in the bulk.[20] For any other angle, the approximation ceases to be exact. In particular, it does not vanish at T_c. Work is in progress to investigate the nature of the contributions mentioned above for general angles. A systematic expansion in $\exp(-4\beta J_x)$ near $\phi=0$, say, may be a possible way to analyze these effects.

It would be grossly unfair to give the impression that SOS is a bad approximation. For the equal coupling case, one can get excellent agreement by taking the SOS from $\phi=0$ to $\pi/4$ and using the fourfold symmetry to get the rest. Although such a ST (σ_{SOS}) would have a kink at $\pi/4$, $\sigma_{\text{SOS}}/\sigma_{\text{exact}}$ as a function of ϕ and T, is within 1% of unity in over half of the region $0 \leq \phi < 2\pi$, $0 \leq T \leq T_c$ in the ϕ-T plane. For the ES, Ref. 18 gave the explicit result also. As expected $y(x)$ becomes infinite at some finite value of x since they employed a formula which is exact at $\phi = \pi/2$. Using this ES up to $dy/dx = 1$, they generate a complete droplet by symmetry. For such a droplet, they also quote the radius of curvature at the corners, which agrees with the exact result up to terms in $\exp(-4\beta J)$. However, we do not understand the nature of such a droplet near T_c: since the true (SOS) ST does not vanish at T_c for any angle except $0, \pm\pi/2, \pi$ yet Burton *et al.* claimed that the droplet becomes circular near T_c, corresponding to an orientation-independent ST.

In conclusion, we point out several directions one may continue future studies. Other $d=2$ models: there is a wealth of models which are "soluable" to various degrees. What type of ES do they produce? Other applications: even within the confines of the $d=2$ Ising ES [the remarkably simple (10)], we are aware of two possible channels of exploration. One is further comparisons with Monte Carlo simulations or with the shapes of nucleation platforms in real crystal growths. The other is a study of the fluctuations about this ES, which enter into the analysis of singularities associated with first-order transitions.[21]

In Refs. 21, the soft fluctuations about a spherical (circular) droplet (ES) are considered since they were concerned with a totally isotropic theory (the ϕ^4 field theory). Near criticality, circular droplets may be a good approximation to the Ising case. Far from criticality, it is the ES of Eq. (10) that enters. We expect that an analysis starting from our ES will produce singularities which are closer to the true Ising ones for all T below T_c. Lastly we believe that this study of ST and ES may be extended to include the effects of an external field, such as gravity. From there, we hope to develop a theory of roughening transitions in the presence of gravitational fields.

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[1]For references on ST, see those in Refs. 8 and 9.

[2]J. D. Weeks, G. H. Gilmer, and H. J. Leamy, Phys. Rev. Lett. 31, 549 (1973); H. J. Leamy, G. H. Gilmer, and K. A. Jackson, *Surface Physics of Materials* (Academic, New York, 1975).

[3]H. J. Leamy and G. H. Gilmer, J. Cryst. Growth 24/25, 499 (1974); H. van Berjeren, Phys. Rev. Lett. 38, 993 (1977) provided an exactly soluable model of a roughening transition.

[4]G. Wulff, Z. Kristallogr. 34, 449 (1901). For a more recent treatment see C. Herring, in *Structure and Properties of Solid Surfaces,* edited by R. Gomer and G. S. Smith (University of Chicago Press, Chicago, 1955).

[5]H. Cheng and T. T. Wu, Phys. Rev. 164, 719 (1967). For a summary see B. McCoy and T. T. Wu, *The Two-Dimensional Ising Model* (Harvard, Cambridge, Mass., 1973), pp. 299–305. See also M. E. Fisher and R. J. Burford, Phys. Rev. 156, 583 (1967), and L. Onsager, Phys. Rev. 65, 117 (1944).

[6]E. W. Montroll, R. B. Potts, and J. C. Ward, J. Math. Phys. 4, 308 (1963).

[7]A. E. Ferdinand, Ph.D. thesis (University of London, 1967) (unpublished), Chap. 11; M. E. Fisher, J. Phys. Soc. Jpn. Suppl. 26, 87 (1969); P. G. Watson, J. Phys. C 1, 575 (1968); and in *Phase Transitions and Critical Phenomena,* edited by C. Domb and M. S. Green (Academic, New York, 1972), p. 116; R. H. Swendsen, Phys. Rev. B 17, 3710 (1978); E. Fradkin, B. A. Huberman, and S. H. Shenken, *ibid.* 18, 4789 (1978); and R. K. P. Zia, Phys. Lett. 64A, 345 (1978).

[8]C. Rottman and M. Wortis, Phys. Rev. B 24, 6274 (1981).

[9]J. E. Avron, L. S. Schulman, H. van Beijeren, and R. K. P. Zia, J. Phys. A 15, L81 (1982).

[10]We denote unit vectors in d-dimensional space by a caret (ˆ). Scalar product is written with a dot (·). Components are denoted by subscripts (e.g., n_i, $i=1, \cdots, d$). Repeated indices are summed.

[11]σ is regarded as a function of d *independent* variables n_k when $\partial_k \equiv (\partial/\partial n_k)$ is written. The projector τ automatically eliminates the spurious (radial) component.

[12]This is a generalization of the $d=2$ case, Eq. (D4) in Ref. 18.

[13]C. Rottman pointed out to us that this formula also appeared in D. W. Hoffman and J. W. Cahn, Surf. Sci. 31, 368 (1972); Acta Metall. 22, 1205 (1974).

[14]A. A. Chernov, Usp. Fiz. Nauk. 73, 277 (1961) [Sov. Phys. Usp. 4, 116 (1961)]. We thank Dr. S. Stoyanov for pointing out this article to us.

[15]We use the notation of M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1965), Chap. 17, for $K(m)$.

[16]K. Binder and M. H. Kalos, J. Stat. Phys. 22, 363 (1980).

[17]We thank Professor K. Binder for providing us with the numerical data that were used to construct Fig. 4 of Ref. 16. Samples have $l \sim 100$ and 500.

[18]H. N. V. Temperley, Proc. Cambridge Philos. Soc. 48, 683 (1952).

[19]W. K. Burton, N. Cabrera, and F. C. Frank, Philos. Trans. R. Soc. London Ser. A 243, 29 (1951).

[20]H. van Beijeren and H. Groenveld (private communication); (unpublished); see also M. E. Fisher and R. J. Burford, Phys. Rev. 156, 583 (1967).

[21]J. S. Langer, Ann. Phys. (N.Y.) 71, 108 (1967); N. J. Gunther, D. A. Nicole, and D. J. Wallace, J. Phys. A 13, 1755 (1980).