INTERFACIAL, BOUNDARY, AND SIZE EFFECTS AT CRITICAL POINTS*

Michael E. Fisher and Arthur E. Ferdinand
Baker Laboratory, Cornell University, Ithaca, New York
(Received 8 May 1967)

Exact results for the interfacial and boundary free energies (for free and for ferromagnetic boundaries) are presented for the square, triangular, and honeycomb Ising lattices. The boundary energies and specific heats diverge as $\ln|T-T_c|$ and $(T_c-T)^{-1}$, respectively. This behavior is interpreted generally in terms of the rounding and displacement of the specific-heat maximum in a finite system.

In view of the recently gained insights into the critical-point behavior of the bulk thermodynamic properties of ferromagnets, fluids, alloys, etc.,[1] it is appropriate to consider in more detail the corresponding interfacial and surface (or boundary) properties and the related distortion of a transition resulting from finite sample size. This last point is relevant to the shifts and rounding of specific-heat peaks observed even in very careful experiments.[2] Although other possibilities must also be considered, the observed effects could be due to the scale of some microcrystalline structure. In this note we report[3] some exact calculations of the interfacial, boundary, and finite size effects for the square-, triangular-, and honeycomb-lattice Ising models.[4] The highly singular nature of the boundary free energy is interpreted in terms of the shift of the specific-heat maximum with size. The probable nature of the critical behavior in real three-dimensional systems is hence indicated.

To explain the principle of our calculations, consider a large square-lattice Ising ferromagnet with nearest-neighbor interactions $J_x = J_1$ and $J_y = J_2$, in the center of which a vertical "ladder" of j horizontal or x bonds have the modified interactions ξJ_1. In general, these perturbed bonds describe a grain boundary whose associated free energy is just the incremental free energy of the pertrubed lattice over the uniform lattice. Evidently, the case $\xi = 0$ describes a free edge (or boundary) of $2j$ sites. [The relative contributions due to the end effects, here and below, are negligible for large j.] Lastly, one can see that the special case $\xi = -1$ corresponds effectively to an interface or domain wall in the uniform lattice, the incremantal free energy now yielding the surface tension. This interface is "pinned" at the ends of the ladder, so that although it may wander statistically, its mean direction is vertical. By perturbing a "staircase" of alternating x and y bonds, diagonal grain boundaries, edges, and interfaces may be described.

A ferromagnetic edge in which all the boundary spins are constrained (e.g., by an infinite local field) to point "up," which in the "lattice gas" corresponds simply to a "hard wall," may be simulated by modifying a chain of j consecutive (say) vertical bonds and letting $\xi J_2 \to \infty$. This ensures that the linked spins always point the same way. Although this direction might be up or down, the resulting two-fold degeneracy is completely negligible thermodynamically. Note, now, that by making a duality transformation[5] on the perturbed lattice for the double free edge, one again describes the pertrubations appropriate to the (double) ferromagnetic edge. [By convention we associate $\frac{1}{2}\times$(bulk free energy per spin) with each "frozen" spin in a ferromagnetic boundary.]

The incremental free energy $\Delta F_j \approx jF^\times$ due to these bond perturbations may be calculated by the Pfaffian methods developed for the Ising and dimer correlation functions[6] and is expressed as the logarithm of a determinant of Toeplitz form and order j (or $2j$). In the cases $\xi \geqslant 0$, the limit $j \to \infty$ is found by treating the matrix as cyclic. For the vertical grain boundary on the square lattice this yields

$$F^\times/kT = \tfrac{1}{2}\ln[(1-\xi'^2 v_1^2)/(1-v_1^2)] - \int_0^{2\pi} \ln[\tfrac{1}{2}(1+\xi') + \tfrac{1}{2}(1-\xi')e^{i\delta(\varphi)}](d\varphi/2\pi), \tag{1}$$

where

$$v_i = \tanh K_i, \quad K_i = J_i/kT, \quad \xi' v_1 = \tanh(\xi K_1),$$

and

$$\delta(\varphi)=\arg\{[1-v_2v_2^+e^{i\varphi}][1-(v_2/v_2^+)e^{-i\varphi}]\}, \quad (2)$$

where

$$\delta\to 0 \text{ as } \varphi\to\pi\pm,$$

and

$$v_2^+=\tanh K_2^+=\exp(-2K_1).$$

The expressions (1) and (2) with $\xi'=0$ also yield (a) the ferromagnetic boundary free energy of the triangular lattice (per pair of spins) for the direction 2 if the first term in (1) is replaced by K_2 and the inversion transformation is extended to[5]

$$\exp(-4K_2^+) = (v_1+v_2v_3)(v_3+v_2v_1)/(v_2+v_1v_3)(1+v_1v_2v_3). \quad (3)$$

By setting $J_3=0$ one then obtains (b) the free energy of a square-lattice vertical ferromagnetic boundary. Alternatively, $J_1=J_x$, $J_2=0$, and $J_3=J_y$ yields the result for (c) a diagonal ferromagnetic boundary on the square lattice. Taking the dual of these expressions confirms (d) the square-lattice vertical free edge result [Eq. (1) with $\xi'=0$] and also yields the free energy of (e) a diagonal free edge on the square lattice. Similarly, the dual of the full triangular-lattice formula gives (f) the free energy of a honeycomb-lattice free edge (normal to the 2 axis). Finally, the dual pair of expressions for (g) a ferromagnetic honeycomb boundary and (h) a free triangular edge have also been obtained.

In the special case $\xi=-1$, needed for the interfacial tension $\sigma(T)$, the relevant Toeplitz determinant is generated directly by $\exp[i\delta(\varphi)]$. Above T_c the Szegö-Kac theorem[6] proves, as expected, that $\sigma(T)$ vanishes identically. Below T_c we may appeal to Wu's analysis.[7] For an interface parallel to the 3 axis of the triangular lattice we find that

$$\sigma_3(T)/kT=\ln[\sinh 2K_1 \sinh 2K_2] +2\ln[\tfrac{1}{2}(1+v_3u_1)^{1/2}+\tfrac{1}{2}(1+v_3u_2)^{1/2}], \quad (4)$$

$$u_1=v_3+(v_1/v_2)+(v_2/v_1), \quad u_2=v_3+v_1v_2+(v_1v_2)^{-1}. \quad (5)$$

When $J_3=0$, the second term in (4) vanishes and the first gives the diagonal surface tension for the square lattice. The square-lattice longitudinal surface tension, first found by Onsager,[8] is recaptured by setting $J_1=0$, $J_2=J_x$, and $J_3=J_y$. The result for the honeycomb lattice[9] may be obtained directly from (4) and (5) by applying the star-triangle transformation.[5] It may be written compactly using (3) as[10]

$$\sigma_3(T)/kT=2(K_3-K_3^+). \quad (6)$$

The critical-point behavior is in all cases the same, namely that $\sigma(T)$ vanishes linearly with (T_c-T). Our calculations for the square-lattice diagonal, however, also indicate that $\sigma(T)$ becomes isotropic close to T_c in the metric described by $r^2=x^2\sinh^2 2K_{y,c}+y^2$.[11] See Fig. 1 for the case $J_x=J_y$, $\sinh 2K_c=1$.

The analysis of the integrals (1) for the boundary free energies is quite involved. One may re-express $F^\times$ generally as an integral over complete elliptic integrals but, in contrast to the bulk free energy, all three kinds are needed in most cases. Our simplest result is for the energy per spin of a free diagonal edge on the square lattice. For $J_x=J_y$ and $T\gtrless T_c$ this is

$$U^\times/J=\tfrac{1}{2}\coth 2K\{\pm 1+(2/\pi)\vec{\mathrm{K}}(k_1)\}, \quad (7)$$

where $k_1=2\tanh 2K \operatorname{sech} 2K$. Hence, we find

$$\frac{U^\times}{\sqrt{2}J}=\frac{-1}{\pi}\ln|t|\pm\tfrac{1}{2}+c_1-\frac{\sqrt{2}K_c}{\pi}t\ln|t|+O(t), \quad (8)$$

as

$$t=(T/T_c)-1\to 0, \quad (9)$$

where c_1 is a constant and $K_c=\frac{1}{2}\ln(1+\sqrt{2})$. As shown in Fig. 1, the boundary energy thus diverges logarithmically. (Such a divergence of the bulk energy is, of course, impossible.) Similarly, the boundary specific heat diverges with a simple pole:

$$\frac{C^\times}{\sqrt{2}k}=-\frac{K_c}{\pi}t^{-1}-\frac{\sqrt{2}K_c^{\,2}}{\pi}\ln|t|+c_2^\pm+O(t\ln|t|), \quad (10)$$

where $c_2^\pm$ are constants. For a longitudinal edge the logarithmic singularity and discontinuity in $U^\times/J$ have the same magnitudes as in (8), again indicating isotropy near T_c. By the transformations explained above it is clear that the same singularities characterize free and ferromagnetic boundaries on all the lattices, except that in the latter case the amplitudes are of opposite sign.

We will now try to relate these striking results to the limited height, rounding, and displacement of the peak of the total specific heat $C_N(T)$ of a finite sample of, say, $N=n_1\times\cdots\times n_d$ spins on a d-dimensional cubic lattice. As re-

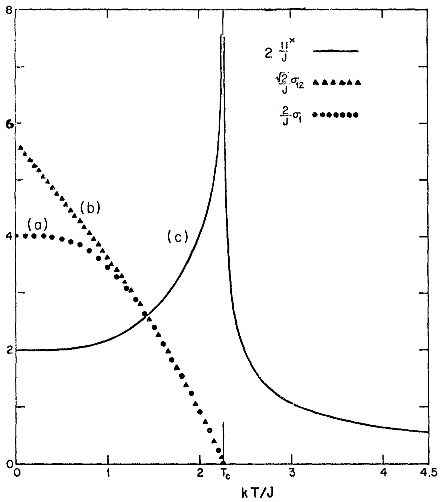

FIG. 1. Plots versus temperature of (a) the longitudinal surface tension, (b) the diagonal surface tension, and (c) the energy per spin of a free boundary for the square Ising lattice.

gards the location of T_{max}, a naive mean-field type of argument for a $d=3$ lattice with free faces indicates that

$$NkT_{max} \propto E_{N,0}$$
$$= J[dN - n_2 n_3 - n_3 n_1 - n_1 n_2 - O(n_1, n_2, n_3)], \quad (11)$$

where $E_{N,0}$ is the ground-state energy and the negative terms arise from loss of binding energy at the surfaces. Since $T_{max} \to T_c$ as $N \to \infty$, this suggests generally that

$$\epsilon = (T_c - T_{max})/T_c$$
$$\approx b d^{-1}(n_1^{-1} + \cdots + n_d^{-1}) = b/\tilde{n} \quad (12)$$

with $b \simeq 1$. [For ferromagnetic boundary conditions one similarly expects $b \simeq -1$.] This dependence on $\tilde{n}$ is borne out by analytic study of finite-plane Ising models for $n_1 \simeq n_2$, while numerical studies yield $b \simeq 1.3$. [For toroidal (periodic) boundary conditions and $n_1 = n_2$ we find $b = -0.35$, the smaller value being in accord with the corresponding naive prediction $b \simeq 0$.[12]]

Analysis of the exact formulas for the free energy of finite-plane Ising lattices as sums over the eigenvalues of appropriate near cyclic matrices[6,13] reveals that the transition rounding derives from the effective truncation at low wave numbers $\vec{q}_0 \simeq (\pi/n_1 a, \pi/n_2 a)$ of the limiting integrals over reciprocal space. The main result is to replace t^2 in the limiting singular terms by

$$t^{*2} = (t+\epsilon)^2 + \delta^2, \quad \delta^2 \approx \tfrac{1}{2}c^2(n_1^{-2} + n_2^{-2}), \quad (13)$$

where $c = O(1)$. Smearing of the singularities thus takes place over a width $\Delta t \simeq \delta$ (the peak being shifted to $t = -\epsilon$). This is consistent with the general interpretation that rounding occurs when the range of correlation $\kappa^{-1}(T)$ attains the magnitude of the mean linear dimensions, say $\bar{n}a = ad^{1/2}(n_1^{-2} + \cdots + n_d^{-2})^{-1/2}$. Assuming[1] that $\kappa(T) \sim |t|^{\nu}$, this suggests a width

$$\delta = \Delta T/T_c \simeq c/\bar{n}^{-1/\nu}. \quad (14)$$

For the plane Ising models, $\nu = 1$, and the width and shift of the peak are of the same magnitude. For $d=3$, however, $1 > \nu > \frac{1}{2}$ is expected[1] so that the width may be much smaller than the shift. A similar conclusion may be reached concerning the effects of impurities, etc. As a fairly wide experimental observation this seems to be correct.[14]

One may hence guess tentatively that the total specific heat of a general finite system near T_c will be well described by[15]

$$C_N(T)/k$$
$$\approx NA_N(|t^*|^{-\alpha} - 1)/\alpha + NB(t+\epsilon, \delta) + \cdots, \quad (16)$$

where t^* is given by (13), B is a bounded function, $\alpha \to 0$ yields a logarithm, and, possibly, $A_N \simeq A[1 + (b'/\tilde{n})]$. For the square Ising lattice ($\alpha = 0$, $\nu = 1$, $A = 8K_c^2/\pi$) substitution of $t = -\epsilon$ and $t = 0$ in this formula leads to the asymptotic relations

$$C_{N,\max}, C_N(T_c)$$
$$= A \ln n_1 + A\{D_m(\eta), D_c(\eta)\} + \cdots \quad (17)$$

as n_1, $n_2 \to \infty$ with $\eta = n_1/n_2$ fixed.[4] This again is confirmed by detailed calculation. Indeed, for torus we have found explicitly

$$D_c(\eta) = \ln(2^{5/2}/\pi) + C_E - \pi/4$$
$$- \frac{\pi\theta_2^2\theta_3^2\theta_4^2}{2\eta(\theta_2+\theta_3+\theta_4)^2} - \sum_{i=2}^{4} \frac{2\theta_i \ln\theta_i}{\theta_2+\theta_3+\theta_4}, \quad (18)$$

where C_E is Euler's constant, $\theta_i = \vartheta_i(0|i/\eta)$ and $\vartheta_i(z|\tau)$ are the elliptic theta functions of modulus $e^{i\pi\tau}$.[16] Corrections to (17) and (18) are $o(n_1^{2-\lambda})$ for any $\lambda > 0$, and invariance under the interchange of n_1 and n_2 is assured by Jacobi's imaginary transformation.[16] Similar asymptotic formulas have been found for the energy and entropy at T_c.

Finally, for $T \neq T_c$ let us expand (16) in powers of ϵ and δ using (12) and (14). In addition to the expected limiting bulk behavior $C_N/N \approx (A/\alpha)(|t|^{-\alpha}-1)$, this yields boundarylike terms proportional, for $d=2$ and 3, to (n_2+n_1) and $(n_2n_3+n_3n_1+n_2n_3)$, respectively, which arise directly from the shift in $T_{\max}$. The corresponding boundary specific heat per spin near T_c is[17]

$$C^{\times}/k \approx -(Ab/2d)\,\mathrm{sgn}\{t\}\,|t|^{-1-\alpha} + (Ab'/4d\alpha)[\,|t|^{-\alpha}-1] + \cdots. \tag{19}$$

For $\alpha = 0$ the leading singularities are just those found explicitly in (10) (including the change of sign for ferromagnetic boundaries when $b < 0$). Comparing the amplitudes of t^{-1} indicates $b = 1/2K_c \simeq 1.135$; this compares not unfavorably with the estimate $b \simeq 1.3$, quoted above.[18] We take this as a confirmation of our over-all picture of the origin of the critical singularities in the boundary free energy and conclude that (19) should provide a fairly reliable general description.

*Research supported in part by the National Science Foundation and the Advanced Research Projects Agency through the Materials Science Center at Cornell University.

[1]See, e.g., Critical Phenomena, edited by M. S. Green and J. V. Sengers (National Bureau of Standards, Washington, D. C., 1967), and forthcoming reviews by L. P. Kadanoff et al., to be published; P. Heller and M. E. Fisher, to be published.

[2]J. Skalyo, Jr., and S. A. Friedberg, Phys. Rev. Letters 13, 133 (1964); D. T. Teaney, Phys. Rev. Letters 14, 898 (1965), and in Ref. 1.

[3]Brief reports of our main conclusions have been presented in an invited lecture at the American Physical Society Meeting in New York, 2 February 1967, and at the Informal Meeting on Statistical Mechanics at Yeshiva University, 6 April 1967.

[4]C. Domb, Proc. Phys. Soc. (London) 86, 933 (1965), has discussed some aspects of the finite size effects from the viewpoint of the high-temperature series expansions.

[5]See C. Domb, Advan. Phys. 9, 149 (1960), Secs. 3.4.2 to 3.4.5.

[6]E. W. Montroll, R. B. Potts, and J. C. Ward, J. Math. Phys. 4, 308 (1963); M. E. Fisher and J. Stephenson, Phys. Rev. 132, 1411 (1963).

[7]T. T. Wu, Phys. Rev. 149, 380 (1966).

[8]L. Onsager, Phys. Rev. 65, 117 (1944). Onsager effectively computes the free energy for a "misfit seam" or "antiphase boundary" in an Ising antiferromagnet. By the spin-inversion symmetries, however, this is easily seen to be identical to the ferromagnetic "domain-wall" free energy which we compute.

[9]The special results for the honeycomb and triangular lattices with $J_1=J_2=J_3$ have been found independently by P. G. Watson, private communication.

[10]This is similar to a formula of Onsager's and, indeed, applies with appropriate definitions also to the triangular and square lattices.

[11]This is the same metric found by L. P. Kadanoff, Nuovo Cimento 44, 276 (1966), to be appropriate for the decay of the pair spin correlations near T_c.

[12]Onsager (Ref. 8) reported $\epsilon \sim n^{-2}\ln n$ but this was for an $n\times\infty$ torus. From the arguments given below one can see that the next correction term in (12) should take such a form.

[13]B. Kaufman, Phys. Rev. 76, 1232 (1949).

[14]See, for example, Teaney's measurements on two MnF_2 crystals (Ref. 2) and B. E. Keen, D. P. Landau, and W. P. Wolf, J. Appl. Phys. 38, 967 (1967), for measurements on three crystals of dysprosium aluminum garnet.

[15]For simplicity we assume that the bulk specific-heat singularity is symmetric, although $B(t+\epsilon,\delta)$ might approach a discontinuous function as $\delta \to 0$.

[16]See, e.g., E. T. Whittaker and G. N. Watson, Modern Analysis (Cambridge University Press, Cambridge, 1927).

[17]Higher order terms can be proportional to $\delta(t)$, e.g., if $B(t',\delta) \propto t'(t'^2+\delta^2)^{-1/2}$. There are also many other possible sources of the second term in (19).

[18]Deviations from this simple relation for b would arise if, for example, the total specific heat were the average of two terms like (16) but with different values of b, since the boundary specific heat and $T_{\max}$ would involve different average b values.