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Nonsymmetric First-Order Transitions: Finite-Size Scaling and Tests for Infinite-Range Models

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Finite-size rounding of first-order transitions is studied for the general case of nonsymmetric phases and nonperiodic boundary conditions. The main features include the surface-induced shift of the rounded transition on the scale $1/L$, while the order parameter discontinuity is rounded on the scale $1/L^d$. This rounding is described by the universal scaling forms with scaling functions identical to those for the periodic, symmetric case. The proposed formalism applies to scalar-order-parameter, single-domain systems. It is tested by exact calculations for a class of infinite-range models.

KEY WORDS: Finite-size scaling; rounded transitions; surface effects; phase coexistence.

1. INTRODUCTION

Recent experimental and numerical Monte Carlo studies have focused interest on finite-system-size effects at first-order phase transitions with no symmetries between the phases and with nonperiodic boundary conditions. Indeed, earlier theoretical developments usually assumed *periodic boundary conditions* and were largely limited to Ising or other ferromagnetic systems with *symmetric phases* (see refs. 1–4 and reviews in Chapters 1, 4, and 5 of ref. 5).

Detailed studies of the scaling forms of the rounded nonsymmetric transitions (with periodic boundary conditions) used the formalism of the probability density of the order parameter.$^{(2,6)}$ Some of the unsolved theoretical issues associated with these studies have been reviewed in Chapter 1 of ref. 5. Ferromagnetic Ising transitions can also become effectively nonsymmetric if the boundary conditions are nonperiodic and involve

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surface fields. Finite-size transition point shifts in the slab geometry were investigated for such systems in ref. 7, by using mean-field type considerations. However, in this paper we consider fully finite systems so that the transition is not only shifted but also *rounded.*$^{(8)}$ Also, we study only the case of scalar order parameter, thus excluding from the consideration soft-mode (spin-wave) effects, which are known to lead to a qualitatively different finite-size behavior.$^{(4)}$

It turns out that the most important boundary condition and geometry effects are associated with the formation of interfaces in the bulk of the finite system (i.e., away from the surfaces). If the interfaces are formed spontaneously, as happens in the long cylindrical geometries,$^{(1,3)}$ or are imposed by the boundary fields of opposite sign,$^{(9)}$ then the system is multidomain and the scaling form of the rounded transition is qualitatively different from the single-domain case.

For single-domain systems, which are considered in this work, it turns out that the scaling form of the rounding is not affected by boundary effects, etc. However, the (rounded) transition is shifted from its bulk (infinite size) value.$^{(8)}$ Most numerical and experimental results have been obtained for single-domain systems. Specifically, nonsymmetric first-order transitions in some $2d$, $q>4$ Potts models (with periodic boundary conditions) were studied by Monte Carlo methods.$^{(6,10)}$ More recent Monte Carlo studies have focused on 2D Ising-type systems in rectangular geometries with *free* and *applied-surface-field* boundary conditions.$^{(11,12)}$ These and other theoretical studies (e.g., refs. 13 and 14) also addressed surface-induced transition point shifts of order $1/L$ in the "slab" (i.e., thin film in 3D) and "strip" (in 2D) geometries,$^{(7)}$ where L is a characteristic system size.

Experimental results available are less definitive. Finite-size rounding and surface-effect-related transition point shifts have been observed in several experiments (e.g., refs. 15–18).[3] Results in 3D$^{(15-17)}$ indicate clear "surface" $1/L$ shifts. However, no fits to the theoretical scaling forms have been attempted. The 2D study of ref. 18 reports the first experimental fit of the rounded-transition data to a scaling form.

In this work we reconsider and systematize (in Sections 2–4) the available theoretical information$^{(2,5,6,8,19-21)}$ on finite-size effects at nonsymmetric first-order transitions (in systems with periodic boundary conditions) and also extend the formulation (in Sections 2 and 3) to allow for nonperiodic boundary conditions.$^{(8)}$ We then test (in Sections 5 and 6) several aspects of the proposed formalism in the case of exactly solvable infinite-range models.

[3] Ref. 18 also provides further references for studies of first-order transitions in adsorbed monolayers.

2. PARTITION FUNCTION NEAR PHASE COEXISTENCE

Coexistence of I discrete phases is marked by their bulk free energies (which we measure per unit volume and per $k_B T$) being equal. Let $f_i^{(b)}(\{J\})$ $(i=1,2,\ldots,I)$ denote these single-phase bulk $(L=\infty)$ free energies, which become equal at $\{J_c\}$, where $\{J\}$ denotes collectively various externally controlled thermodynamic variables such as the applied field H, the temperature T, etc. We assume *large finite* systems in the sense that $\infty > L \gg \xi_i^{(b)}$, with $\xi_{i=1,\ldots,I}^{(b)}$ denoting the bulk single-phase correlation lengths, which are finite near and at $\{J_c\}$, because we do not consider systems with soft modes due to continuous symmetries.$^{(4)}$ As emphasized in Section 1, for a large class of boundary conditions the most probable configurations are single domain, i.e., if any interfaces exists, they are bound near the surfaces and do not "unbind" into the bulk of the finite sample. We consider only such systems here (see refs. 1, 3, 5, and 9 for other possibilities and for further references). The "single-domain" property does not imply that the multiphase configurations are not possible, but that the "uniformly magnetized" states dominate the partition function sum; see, e.g., refs. 1 and 5.

Let V denote the finite system volume, so that we can conveniently put

$$V = L^d \tag{2.1}$$

With the above conventions and assumptions, it is natural to consider the following phenomenological expression for the partition function Z near $\{J_c\}$:

$$Z \simeq \sum_{i=1}^{I} e^{-Vf_i(\{J\},L)} \tag{2.2}$$

where the L dependence of the free energies also implicitly indicates the boundary condition, shape, and other geometrical feature dependences. We generally expect that

$$\lim_{L\to\infty} f_i(L) = f_i^{(b)} \tag{2.3}$$

A replacement of $f_i(L)$ by $(f_i^{(b)} + \text{corrections})$ in (2.2) is a natural step in deriving the finite-size scaling behavior. It is therefore important to investigate the form of these finite-L corrections, i.e., the L dependence of the differences

$$\Delta f_i = f_i(L) - f_i^{(b)} \tag{2.4}$$

These differences may be viewed as sources of "prefactors" in the sum of terms of the form $\exp(-Vf_i^{(b)})$ [compare (2.2)]. Such finite-size prefactors will be discussed in detail in Sections 3, 4, and 6.

Before addressing this issue, it is useful to remark on yet another technical point related to (2.2). Each bulk free energy $f_i^{(b)}$ is, strictly speaking, defined only for the range of parameters $\{J\}$ for which the ith phase is stable (i.e., when this free energy is minimal, at least, in the mean-field description). Extension of the thermodynamic definition to the metastable regions is hampered by essential singularities (see, e.g., refs. 22–25). However, as emphasized in Chapter 1 of ref. 5, in finite-size analysis one only uses the first few terms of the expansion of $f_i^{(b)}(\{J\})$ near $\{J_c\}$, so that the problem of the continuation does not really arise, because one essentially manipulates polynomials in $\{J-J_c\}$.

In order to avoid notational complications, we will consider only the case of the two-phase coexistence, i.e., we take $I=2$ in the remainder of this work. Extensions to $I>2$ are quite straightforward, but cumbersome, and the two-phase case is sufficient to illustrate all the important aspects of the formalism. It is convenient to use a magnetic-type notation. Thus, we single out one parameter h from the set $\{J-J_c\}$ such that h can be regarded as an "applied field" variable driving the system through a first-order transition at $h=0$, between the two phases $i=1$ and $i=2$. Near $h=0$, we can expand

$$f_1^{(b)}(h)=f_0^{(b)}-m_1^{(b)}h+\tfrac{1}{2}\chi_1^{(b)}h^2+\cdots \tag{2.5}$$

$$f_2^{(b)}(h)=f_0^{(b)}-m_2^{(b)}h+\tfrac{1}{2}\chi_2^{(b)}h^2+\cdots \tag{2.6}$$

where, as mentioned, these series are not convergent, but this causes no difficulties in finite-size scaling relation derivations. [Thermodynamic definitions of the "field" h appropriate for various systems and ensembles were described, e.g., in ref. 21.]

3. SURFACE AND BOUNDARY EFFECTS

The free-energy quantities entering in the exponentials in (2.2) were not defined precisely. However, *away from the phase transition* we expect the contribution of the stable phase, say, $i=i_0$, to dominate the partition function. The finite-size contributions to the single-phase free energy away from any phase transition point can be understood in terms of the standard bulk–surface–edge (in 3D)–corner terms.[26] Thus, for periodic boundary conditions the difference in (2.4) is exponentially small,

$$\Delta f_{i_0}\sim e^{-L/\xi_{i_0}}\qquad \text{(periodic)} \tag{3.1}$$

For free or fixed boundary conditions as well as for most other "single-domain" nonperiodic boundary conditions, the leading finite-size correction will be of the form

$$\Delta f_{i_0}(h, L) = \frac{\varphi_{i_0}(h)}{L} + O\left(\frac{1}{L^2}\right) \qquad \text{(nonperiodic)} \tag{3.2}$$

where $\varphi_{i_0}(h)$ is proportional to the surface free energy density, while higher-order terms [not shown explicitly in (3.2)] can be associated with geometrical features such as edges, corners, surface curvature, etc.: see Chapter 1 of ref. 5 for a detailed review. To be more specific, consider the case of a finite sample of surface area S, and assume that the boundary conditions (boundary fields, etc.) are uniform over the surface. The ratio $s \equiv V^{(d-1)/d}/S \equiv L^{d-1}/S$ depends only on the system shape. The surface free energy density (per unit area and per $k_B T$) of the ith phase, which is a "local" surface property, is then $s\varphi_i$, provided $\varphi_i(h)$ is defined as in (3.2).

Based on studies for periodic boundary conditions$^{(1,2,5,19,20)}$ (see below), we conjecture that the forms like (3.1) and (3.2) for $\Delta f_i(h, L)$ apply also near and at $h = 0$. More specifically, we argue that the leading finite-size rounding for systems with surfaces can be described by replacing the free energy functions $f_i(h, L)$ in (2.2) by

$$f_i(h, L) \simeq f_0^{(b)} - m_i^{(b)} h + \frac{\varphi_i(0)}{L} \tag{3.3}$$

where the accuracy can be improved by keeping a finite number of terms of higher order in h and $1/L$.

At this point we note that the discussion in this section has been quite general, and the fact that $I = 2$ was not implemented except in using h instead of more general system parameters $\{J - J_c\}$. However, in our derivation of explicit scaling results we will assume $I = 2$ to avoid overly cumbersome expressions. Furthermore, without loss of generality we assume that $m_2^{(b)} > m_1^{(b)}$, so that phase 1 is stable for $h < 0$. We introduce the notation

$$\mu \equiv \tfrac{1}{2}(m_2^{(b)} - m_1^{(b)}) \tag{3.4}$$

$$\bar{m} \equiv \tfrac{1}{2}(m_2^{(b)} + m_1^{(b)}) \tag{3.5}$$

$$h_c = h_c(L) \equiv \frac{\varphi_2(0) - \varphi_1(0)}{L(m_2^{(b)} - m_1^{(b)})} \tag{3.6}$$

With these conventions, substitution of (3.3) in relation (2.2) yields for the free energy near $h=0$ the result

$$f(h, L) \equiv -\frac{1}{V}\ln Z \simeq f_0^{(b)} + \frac{\varphi_2(0)+\varphi_1(0)}{2L} - \bar{m}h - \frac{1}{V}\ln\{2\cosh[\mu(h-h_c)\,V]\} \tag{3.7}$$

Thus, in addition to the (trivial) additive free energy surface correction of order $1/L$, there is also *the surface-induced shift* $h_c(L)$ *in the scaling part*, which describes the rounded kink in the free energy as a function of h. The average order parameter density $m(h, L)$ follows from (3.7) as

$$m(h, L) \equiv -\partial f/\partial h \simeq \bar{m} + \mu\tanh\{\mu[h-h_c(L)]\,V\} \tag{3.8}$$

In this leading order of the scaling description, the order parameter discontinuity $m_2^{(b)} - m_1^{(b)} \equiv 2\mu$ is rounded on the scale $\sim 1/V$. Surface effects cause the shift$^{(8)}$ of order $1/L$, but the shape of the rounded order parameter, i.e., the hyperbolic-tangent scaling function, is the same as was found for symmetric periodic Ising models.$^{(1-3,5)}$ It is interesting to note that Hill's thermodynamic "equal area rule" definition$^{(21)}$ of the rounded transition shift is equivalent to (3.6) in the leading order $(1/L)$.

4. PERIODIC BOUNDARY CONDITIONS

For systems with periodic boundary conditions the considerations of Section 3 suggest that in the expression for the partition function near the transition the exponentials of the bulk free energy add up with no prefactors,

$$Z \simeq \sum_{i=1}^{I} \exp[-Vf_i^{(b)}(\{J\})] \qquad \text{(periodic).} \tag{4.1}$$

This is a rather surprising conclusion, and its implications are that there is no shift in the rounded transition in the case $I=2$ (only), and that the only power-law finite-size free-energy correction at $h=0$ is the $-V^{-1}\ln 2$ term which separates out of the logarithm in (3.7). [In fact, for nonperiodic boundary conditions it should be dropped in a consistent $O(1/L)$ approximation.] For general I, this correction at $\{J_c\}$ is given by $-V^{-1}\ln I$. As reviewed in Chapter 1 of ref. 5, the validity of the "no prefactor" property has been established by transfer matrix$^{(19)}$ (for $I=2$) and rigorous$^{(20)}$ methods.

A detailed study of the finite-size behavior at first-order transitions can be also conducted within the formalism of the probability distribution $P(M)$ of the fluctuating overall order parameter density M.(2,6) Note that the thermodynamic average value of M is the order parameter m encountered in (3.8), etc. For $h \simeq 0$, the function $P(M)$ is sharply peaked at the M values near $m_1^{(b)}$ and $m_2^{(b)}$. The precise form of the peaks and of $P(M)$ generally, has been extensively investigated (see, e.g., ref. 27). However, it is less clear how to "add up" two competing peaks. One approach(2) is to add them up with such coefficients that the areas under the peaks are equal at $h=0$ (for the nonperiodic case, at h_c). This yields the "no prefactor" partition function.

One can offer another line of argument(6) based on a certain mean-field intuition, which leads to a partition function expression with extra prefactors. We do not detail these considerations here, nor the attempts to reconcile both approaches by allowing for finite-size corrections in $P(M)$ (see ref. 5 for details). It is important to point out, however, that the formulation of ref. 6 would suggest an additional shift in the transition, for *periodic boundary conditions*, proportional to $V^{-1} \ln(\chi_2^{(b)}/\chi_1^{(b)})$. This shift would be rather small unless the transition is extremely nonsymmetric (so that the susceptibilities differ by several orders of magnitude). The use of the resulting scaling expressions to fit Monte Carlo data for Potts models(6,10) showed no inconsistencies.

Thus, although we believe that the "no prefactors" partition function is the correct answer, the final resolution of the controversy must await a reanalysis of the Monte Carlo data. Some of the features of the probability distribution for M will be clarified by exact calculations for infinite-range models in Section 6. Finally, we mention that controversies with prefactors for exponentiated free-energy quantities also arise in transfer matrix studies.(3,19)

5. INFINITE-RANGE MODELS: DEFINITION

Consider an infinite-range model of V Ising spins $\sigma_\alpha = \pm 1$. The model has no geometry and therefore the number of spins plays the role of the volume. Thus, we use the notation V, so that, formally, various thermodynamic definitions and expressions obtained in Sections 2–4 remain unchanged. However, densities will be *per spin* instead of *per unit volume*. The configurational interaction energy of an infinite-range model is a function of

$$M = V^{-1} \sum_{\alpha=1}^{V} \sigma_\alpha \tag{5.1}$$

and is assumed to be of the form $E(M) - hM$ (measured per $k_B T$). Note that M can take on a discrete set of values, $M = (2\beta - V)/V$, where $\beta = 0, 1,..., V$.

The partition function of the model can be evaluated be summing over the allowed M values, with the appropriate multiplicity factor $\binom{V}{\beta}$ counting the configurations with a given M. It is convenient to define the quantity $\Omega(M, V)$ via

$$e^{-V\Omega} \equiv \binom{V}{\beta} \equiv V! \Big/ \left[\left(\frac{1-M}{2} V \right)! \left(\frac{1+M}{2} V \right)! \right] \tag{5.2}$$

The following expansion can be easily derived:

$$\Omega = \frac{1+M}{2} \ln \frac{1+M}{2} + \frac{1-M}{2} \ln \frac{1-M}{2} + \frac{\ln V}{2V}$$
$$+ \frac{\ln[(1-M^2)/2\pi^{-1}]}{2V} + \frac{3+M^2}{12(1-M^2)\, V^2} + O[V^{-4}(1-M^2)^{-3}] \tag{5.3}$$

Although we cared to show the "dangerous" behavior of this expansion near $M = \pm 1$, it is actually of no importance, since we will be interested in M values near $m_{1,2}^{(b)}$ which should be in $(-1, 1)$. The partition function takes the form

$$Z = \frac{1}{\sqrt{V}} \sum_M e^{-V[U(M) - hM + u(M)/V]} \{1 + O(V^{-1})\} \tag{5.4}$$

where the bulk potential is defined by

$$U(M) \equiv \Omega(M, \infty) + E(M) \tag{5.5}$$

while the leading correction can be read off (5.3),

$$u(M) = \frac{1}{2} \ln \frac{1-M^2}{2\pi^{-1}} \tag{5.6}$$

Since the energy $E(M)$ is basically arbitrary, and other quantities [such as $u(M)$] are also dependent on the type of the model,(21) we will keep the functions $U(M)$ and $u(M)$ general in what follows. For the bulk potential $U(M)$, however, we assume minima at $M = m_{1,2}^{(b)}$ such that

$$U(M \simeq m_i^{(b)}) = f_0^{(b)} + \frac{1}{2\chi_i^{(b)}} (M - m_i^{(b)})^2 + O[(\Delta m)^3] \tag{5.7}$$

and $U(M) > f_0^{(b)}$ for $M \neq m_{1,2}^{(b)}$. In the following section, we will put $f_0^{(b)} = 0$ for simplicity. We will not discuss explicitly the additive higher order terms

$\sim 1/V$, etc., in (5.4), which contribute $O(V^{-2})$ terms in the thermodynamic quantities, for which the leading finite-size corrections in this case turn out$^{(1,21)}$ to be of order $1/V$.

6. INFINITE-RANGE MODELS: RESULTS

In the preceding section we reduced the evaluation of the partition function of the infinite-range model to summation over M, and identified the leading finite-size terms: see (5.4). Here we consider the finite-size properties near $h=0$. First, we note that the probability of finding the magnetization value M is proportional to the exponential term in the summand in (5.4). It shows explicitly the double-peak structure near $h=0$. To the leading order in h and $1/V$, the sum in (5.4) can be evaluated by keeping (adding up) the two contributions from $M \simeq m_{1,2}^{(b)}$. Each one of these can in turn be evaluated by: (1) using the expansion (5.7); (2) turning the sums into integrals; (3) extending the integration to $\pm\infty$. Thus, we have

$$Z \simeq \frac{\sqrt{V}}{2} \sum_{i=1}^{2} \int_{-\infty}^{+\infty} dM \exp\left\{-V\left[\frac{(M-m_i^{(b)})^2}{2\chi_i^{(b)}} - hM + \frac{u(m_i^{(b)})}{V}\right]\right\} \tag{6.1}$$

As anticipated, the result comes out in the form (2.2), with $I=2$, where the small-h and $1/V$ form of the free energies is

$$f_i(h, V) \simeq -m_i^{(b)} h + \frac{u(m_i^{(b)}) - (1/2)\ln(\pi\chi_i^{(b)}/2)}{V} \tag{6.2}$$

which shows that the leading finite-V correction is indeed of order $1/V$ here [compare with (3.3)].

Next we introduce notation identical to (3.4), (3.5). However, we replace (3.6) by

$$h_c = h_c(V) \equiv \frac{u(m_2^{(b)}) - u(m_1^{(b)}) + (1/2)\ln(\chi_1^{(b)}/\chi_2^{(b)})}{V(m_2^{(b)} - m_1^{(b)})} \tag{6.3}$$

The resulting expression for the free energy [compare (3.7)] reads

$$\begin{aligned} f(h, V) \simeq{}& \frac{u(m_1^{(b)}) + u(m_2^{(b)}) - (1/2)\ln(\pi^2\chi_1^{(b)}\chi_2^{(b)}/4)}{2V} - \bar{m}h \\ &- \frac{1}{V}\ln\{2\cosh[\mu(h-h_c)\,V]\} \end{aligned} \tag{6.4}$$

For the order parameter, relation (3.8) is obtained, with $h_c(V)$ in place of

$h_c(L)$. Finally, one can also check by explicit calculation that the two peaks of the function $P(M)$ have *equal areas* exactly at $h = h_c(V)$.

In summary, the scaling theory for nonsymmetric first-order transitions, incorporating finite-size corrections due to surfaces or other effects, is similar to that for the symmetric case. The main qualitative difference is the shift in the rounded transition, which is directly related to the single-phase, finite-size free energy corrections. These phenomenological observations are fully confirmed by our exact calculations for infinite-range models.

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