Finite-size scaling at first-order phase transitions

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Using thermodynamic fluctuation theory, we study the finite-size rounding of anomalies occurring at first-order phase transitions of the corresponding infinite system. Explicit expressions for thermodynamic functions are derived both for "symmetric transitions" (such as the jump of the spontaneous magnetization in the Ising model from $+M_{sp}$ to $-M_{sp}$ as the field changes from 0^+ to 0^-) as well as for asymmetric cases, but restricting attention to (hyper)cubic system shapes. As an explicit example for the usefulness of these considerations in Monte Carlo simulations where it may be a problem to (i) locate a phase transition and (ii) distinguish first-order from second-order transitions, we present numerical results for the two-dimensional nearest-neighbor Ising ferromagnet in a field, both below the critical temperature T_c and at T_c. The numerical results are found to be in very good agreement with the phenomenological theory and it is shown that one may extract the magnitudes of jumps occurring at first-order phase transitions in a well-defined and accurate way.

I. INTRODUCTION

Finite-size scaling theory[1,2] has become a powerful and well-established tool for the studies of second-order phase transitions (see Refs. 3 and 4 for reviews). More recently finite-size effects at first-order phase transitions also have found attention.[4–10] While finite-size scaling concepts for second-order phase transitions have been applied in Monte Carlo simulations as a standard tool,[11–16] none of the predictions regarding finite-size effects at first-order transitions have been tested by Monte Carlo methods so far. On the other hand, the precise location of first-order phase boundaries with Monte Carlo methods has been a long-standing problem in the literature (for some recent discussions see, e.g., Refs. 16–20). Particularly cumbersome is the accurate estimation of jumps at phase transitions which are only weakly of first order—then even the distinction from second-order transitions may be a problem.[19,20]

We illustrate the difficulty by discussing qualitatively the rounding of the magnetization jump in the Ising ferromagnet as the field is varied (see Fig. 1).[21] In an infinite system, the magnetization jumps from $+M_{sp}$ as $H \to 0^+$ to $-M_{sp}$ reached for $H \to 0^-$. In a system with all linear dimensions L finite, however, no singularities can occur and the variation of the magnetization $\langle S \rangle_L$ with field H is perfectly smooth. Rather than the infinitely steep variation of $\langle S \rangle_L$ with H from $H=0^-$ to $H=0^+$ occurring for $L \to \infty$ (δ-function singularity of the susceptibility in the infinite system), $\langle S \rangle_L$ has a large but finite slope (of order $M_L^2 L^d / k_B T$, see Sec. II) for a finite region of fields ($-M_L L^d / k_B T \lesssim H \lesssim M_L L^d / k_B T$, see Sec. II). Here $\pm M_L$ are the values of the magnetizations where the probability distribution $P_L(s)$ at zero field is maximal, and d is the system's dimensionality.

These considerations already show that one needs to extrapolate from the smooth behavior of the finite system suitably towards $L \to \infty$, in order to estimate the parameter at which the transition occurs (in our case the field $H=0$) as well as the jump of the considered quantity (in our case the magnetization jump $2M_{sp}$). While in the simple Ising case the spin-inversion symmetry

$$H, \{S_i\} \to -H, \{-S_i\} \tag{1}$$

of the Hamiltonian

$$\mathcal{H}_{\rm Ising} = -J \sum_{\langle i,j \rangle} S_i S_j - H \sum_i S_i , \quad \{S_i = \pm 1\} \tag{2}$$

leads to $\langle S \rangle_L = 0$ for $H=0$ independent of L, and hence there is no *shift* of the transition field with size, in more general cases there will be both a rounding and a shift of the transition, and hence the extrapolation towards $L \to \infty$ is nontrivial.

The problem is even more complicated since a Monte Carlo simulation represents a numerical realization of a dynamical stochastic model described by a Master equation[12] (Glauber kinetic Ising model[22] in our example). It may be hard to observe the correct thermal equilibrium behavior discussed so far; instead, the system stays during most of the observation time in the vicinity of one peak of $P_L(s)$, and hence one rather observes a metastable branch. The limit of metastability, but even the magnetization in the metastable branch itself, may then exhibit some systematic dependence on the observation time—note that the first-principle theory of metastability is still a largely unsolved problem of statistical mechanics.[23] Only for

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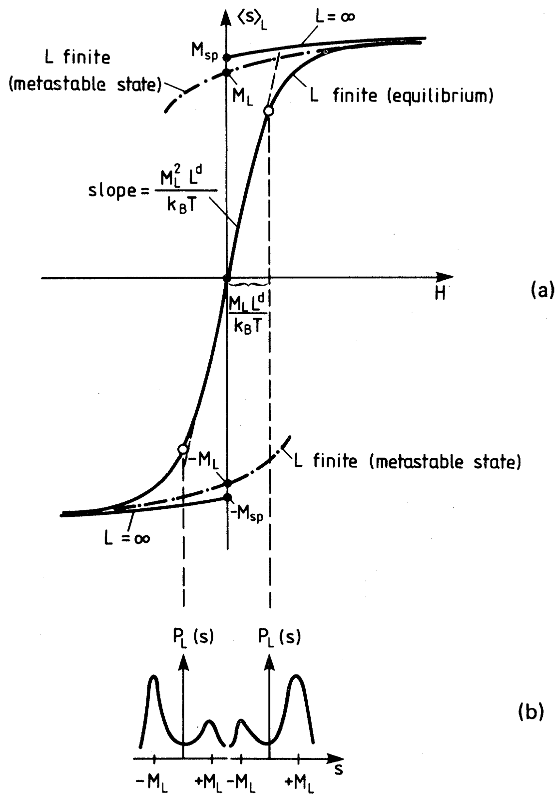

FIG. 1. (a) Variation of magnetization $\langle s \rangle_L$ in a finite Ising ferromagnet plotted vs magnetic field, as observed in thermal equilibrium (full curve) and in a Monte Carlo simulation with sufficiently short observation time where metastable branches (dash-dotted line) occur. The behavior of the infinite system is also indicated (schematic). $\pm M_{\text{sp}}$ is the spontaneous magnetization of the infinite system, $\pm M_L$ is the most probable value of the magnetization in the finite system at $H=0$. (b) Schematic probability distribution $P_L(s)$ of the magnetization for two cases [open circles in (a)] where the magnetization is in between $\pm M_L$.

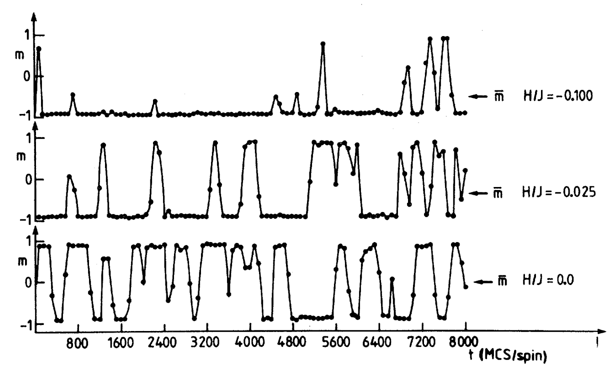

FIG. 2. Time evolution of the magnetization $m(t)$ plotted vs observation time t [measured in Monte Carlo steps (MCS)/spin] in an Ising nearest-neighbor square lattice of linear dimension $L=6$ with periodic boundary conditions at a temperature $k_BT/J=2.1$ (note $k_BT_c/J \cong 2.269$) for three values of the field H. Time averages $\overline{m}$ of $m(t)$ are then estimates of $\langle s \rangle_L$ and are indicated by arrows.

small L is it easy to see many transitions from $+M_L$ to $-M_L$ and vice versa occurring (Fig. 2), and then one can sample the correct distribution $P_L(s)$ and the equilibrium magnetization

$$\langle s \rangle_L = \int_{-1}^{+1} ds\, sP_L(s) \ . \tag{3}$$

In the present work, we wish to demonstrate that in spite of these difficulties one can understand the finite-size effects seen in simulations of first-order transitions quantitatively. Hence, one can use finite-size scaling theory of first-order phase transitions to locate phase boundaries and reliably estimate "jumps" (areas under δ-function singularities, such as the latent heat in a first-order transition driven by temperature variation) not only in principle, but in practice.

We start by working out a phenomenological theory of finite-size effects at first-order phase transitions by a slight generalization of our previous discussion of the probability distribution $P_L(s)$ in Ising models below T_c.[15,24] The results of our approach are not only in agreement with renormalization-group argumets[4,6,7] based on the concept of the description of a first-order transition by a "discontinuity fixed point,"[25] but yield also explicit predictions for the associated finite-size scaling functions. Section III then presents our numerical calculations for Ising square lattices in a field below T_c and compares the results to our theoretical predictions. As a contrast, finite-size scaling in a magnetic field *at* T_c is studied in Sec. IV, and it is shown that first- and second-order transitions are easily distinguished, even though the scaling powers γ/ν $(=\frac{7}{4})$ and $(\gamma+\beta)/\nu$ $(=\frac{15}{8})$ (associated with finite-size scaling in the two-dimensional Ising model at T_c) are only slightly smaller than the scaling power d $(=2)$ associated with the first-order transitions. Section V then generalizes the treatment of Sec. II, which was restricted to the "symmetric" case [cf. Fig. 1 and Eq. (1)], to more general asymmetric situations. Numerical studies of asymmetric first-order transitions, such as those occurring in q-state Potts models for $q>4$ in $d=2$, will be presented in a later publication. Section VI contains finally our conclusions.

II. FINITE-SIZE SCALING IN ISING SYSTEMS BELOW T_c

We start recalling the double Gaussian approximation of Ref. 15 for the probability distribution of the magnetization of an Ising system below T_c at zero field,

$$P_L(s) = \tfrac{1}{2} L^{d/2} (2\pi k_B T \chi_{(L)})^{-1/2} \times \{ \exp[-(s-M_L)^2 L^d/(2k_BT\chi_{(L)})] + \exp[-(s+M_L)^2 L^d/(2k_BT\chi_{(L)})] \} \ . \tag{4}$$

Equation (4) should be accurate when L exceeds distinctly the correlation length ξ at $H=0^+$ (or $H=0^-$) in the infinite system (which below T_c is easy to achieve, as ξ then stays finite); in this limit $\chi_{(L)}$ is well approximated by $\chi=\chi_{(\infty)}$, the susceptibility of the infinite system (at $H=0^+$ or $H=0^-$, respectively), and M_L can be replaced by the spontaneous magnetization M_{sp}. Note that $\chi_{(L)}$ describes the susceptibility of the finite system staying in one ordered phase only; it should not be confused with the total susceptibility χ_L (introduced below) which also contains fluctuations where the system jumps back and forth between the two ordered phases.

The generalization to nonzero field H then simply is (A is a normalization constant)

$$P_L(s)=A(\exp\{-[(s-M_{sp})^2-2\chi sH]L^d/2k_BT\chi\} + \exp\{-[(s+M_{sp})^2-2\chi sh]L^d/2k_BT\chi\}) \ . \quad (5)$$

An alternative formulation is obtained in terms of a free energy per spin f as

$$P_L(s)\propto \exp(-fL^d/k_BT) \ , \quad (6)$$

where, away from T_c, f can be described in terms of a (generalized) Landau theory as (f_0 is some constant)

$$f=f_0+(r/2)s^2+(u/4)s^4-sH \ . \quad (7)$$

A standard calculation yields M as the solution of

$$\frac{\partial f}{\partial s}=rs+us^3-H=0 \ ,$$

i.e., $\pm M_{sp}=\pm\sqrt{-r/u}$ for $H=0$, and linearization around M_{sp} for $H\neq 0$ yields $\chi^{-1}=r+3uM_{sp}^2$. Rewriting Eq. (7) in terms of M_{sp},χ instead of r,u yields (f'_0 is another constant)

$$f=f'_0+\frac{1}{8M_{sp}^2\chi}(M_{sp}^2-s^2)^2-sH \ . \quad (8)$$

Near $s=M_{sp}$ Eq. (8) yields

$$f\approx f'_0+(2\chi)^{-1}(M_{sp}-s)^2-sH \ ,$$

while near $s=-M_{sp}$ Eq. (8) yields instead

$$f\approx f'_0+(2\chi)^{-1}(M_{sp}+s)^2-sH \ .$$

This fact implies that near the peaks of the distribution $P_L(s)$ the formulation in terms of the free energy, Eq. (6), and the double Gaussian approximation are identical. In between the two peaks neither of these expressions is accurate, since there $P_L(s)$ reflects interfacial contributions,[15] but since $P_L(s)$ there is very small, one obtains only negligibly small corrections to $\langle s\rangle_L$, $\langle s^2\rangle_L$, etc. from this regime.

Since the normalization constant A in Eq. (5) can be written as

$$A=\tfrac{1}{2}L^{d/2}(2\pi k_BT\chi)^{-1/2}\exp\left[-\frac{\chi H^2L^d}{2k_BT}\right]\Big/\cosh\left[\frac{HM_{sp}L^d}{k_BT}\right] , \quad (9)$$

we can rewrite Eq. (5) as

$$P_L(s)=\tfrac{1}{2}L^d\frac{(2\pi k_BT\chi)^{-1/2}}{\cosh(HM_{sp}L^d/k_BT)}\left[\exp\left[\frac{HM_{sp}L^d}{k_BT}\right]\exp\left[-\frac{(s-M_{sp}-\chi H)^2}{2k_BT\chi}L^d\right] + \exp\left[-\frac{HM_{sp}L^d}{k_BT}\right]\exp\left[-\frac{(s+M_{sp}-\chi H)^2}{2k_BT\chi}L^d\right]\right] . \quad (10)$$

Thus $P_L(s)$ still is a superposition of two Gaussians, now centered around the shifted magnetization $\pm M_{sp}+\chi H$, as expected. The relative weights of the two peaks are no longer equal as in Eq. (4), however, but rather proportional to $\exp[HM_{sp}L^d/(k_BT)]$ and $\exp[-HM_{sp}L^d/(k_BT)]$, respectively.

From Eq. (10) it is now easy to obtain the moments $\langle s^k\rangle_L$ of interest. The first moment $\langle s\rangle_L$ considered in Fig. 1 becomes

$$\langle s\rangle_L=\chi H+M_{sp}\tanh\left[\frac{HM_{sp}L^d}{k_BT}\right] . \quad (11)$$

We conclude that for $HM_{sp}L^d/k_BT\gg 1$ we simply have the bulk behavior

$$\langle s\rangle_L\approx\chi H+M_{sp} \ . \quad (12a)$$

while in the inverse limit $HM_{sp}L^d/k_BT\ll 1$ we find

$$\langle s\rangle_L\cong\chi H+HM_{sp}^2L^d/(k_BT) \cong HM_{sp}^2L^d/(k_BT) \ . \quad (12b)$$

These results have been anticipated in Fig. 1. It follows hence that the width ΔH over which the transition is rounded is of the order of

$$\Delta H_{round}\approx k_BT/(M_{sp}L^d) \ , \quad (13)$$

because H has to exceed this value to find the behavior characteristic of the infinite system, Eq. (12a). The susceptibility of the finite system χ_L becomes

$$\chi_L\equiv(\partial\langle s\rangle_L/\partial H)_T =\chi+M_{sp}^2L^d\Big/\left[k_BT\cosh^2\left[\frac{HM_{sp}L^d}{k_BT}\right]\right] , \quad (14)$$

which shows that instead of the δ-function singularity at $H=0$ we now have a smooth peak of height proportional to L^d. The only scaling power of L which enters in $\langle s\rangle_L$, χ_L, etc. comes in simply via the volume L^d of the system. This result agrees with previous approaches.[5-10] Of course, it is easy to show that

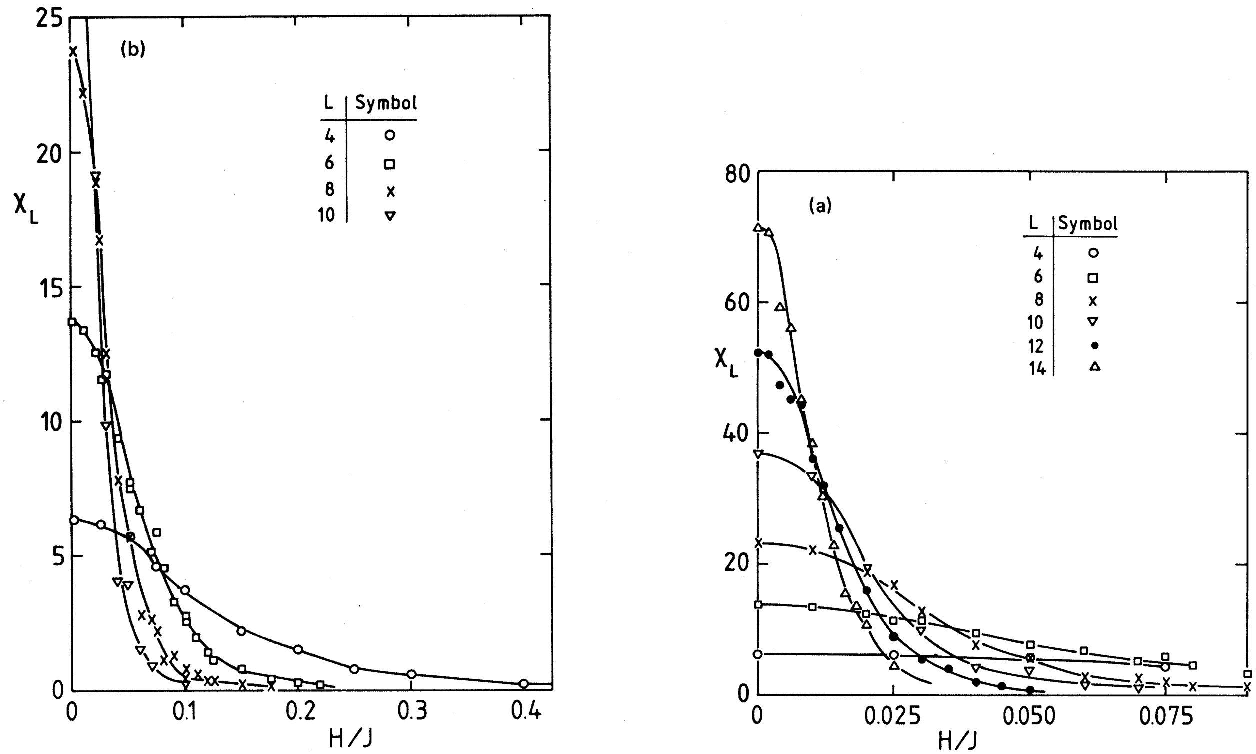

FIG. 3. (a) Susceptibility χ_L plotted vs magnetic field H at $k_BT/J=2.1$ for various L. (b) For the smaller systems the data are replotted on different scales.

$$\langle s^2\rangle_L = M_{sp}^2+\chi^2H^2+\frac{k_BT\chi}{L^d}+2M_{sp}\chi H\tanh\left[\frac{HM_{sp}L^d}{k_BT}\right], \tag{15}$$

and hence the fluctuation relation

$$\langle s^2\rangle_L-\langle s\rangle_L^2=k_BT\chi_L/L^d \tag{16}$$

holds as usual. Higher-order cumulants are then obtained as

$$\langle s^3\rangle_L-3\langle s^2\rangle_L\langle s\rangle_L+2\langle s\rangle_L^3=2M_{sp}^3\left[\tanh^3\left[\frac{HM_{sp}L^d}{k_BT}\right]-\tanh\left[\frac{HM_{sp}L^d}{k_BT}\right]\right] \tag{17}$$

and

$$\begin{aligned}\langle s^4\rangle_L^{\rm con}&\equiv\langle s^4\rangle_L-3\langle s^2\rangle_L^2-4\langle s\rangle_L\langle s^3\rangle_L+12\langle s^2\rangle_L\langle s\rangle_L^2-6\langle s\rangle_L^4\\&=-6M_{sp}^4\left[\left[1-\tanh^2\frac{HM_{sp}L^d}{k_BT}\right]^2-\frac{2}{3}\left[1-\tanh^2\frac{HM_{sp}L^d}{k_BT}\right]\right].\end{aligned} \tag{18}$$

The reduced fourth-order cumulant U_L (sometimes also called the renormalized coupling constant[26]) then becomes

$$U_L=-\frac{\langle s^4\rangle_L^{\rm con}}{3(\langle s^2\rangle_L)^2}=2\frac{[1-\tanh^2(HM_{sp}L^d/k_BT)]^2-\frac{2}{3}[1-\tanh^2(HM_{sp}L^d/k_BT)]}{[1+\chi^2H^2/M_{sp}^2+k_BT\chi/M_{sp}^2L^d+\frac{2\chi H}{M_{sp}}\tanh(HM_{sp}L^d/k_BT)]^2}. \tag{19}$$

It is seen that this quantity goes to $U_L=\frac{2}{3}$ for $H=0$ (Ref. 15) while $U_L\to 0$ for large L when $H\neq 0$. At a second-order transition in contrast, U_L approaches a nontrivial value in between these two limits.[15] Studying the value to which the maximum of $U_L(H)$ converges when $L\to\infty$ can also serve to distinguish between second- and first-order transitions and to locate the field H at which the transition occurs.

III. NUMERICAL EXAMPLE: ISING NEAREST-NEIGHBOR FERROMAGNETIC SQUARE LATTICE

Monte Carlo simulations were performed using a single spin-flip algorithm for square Ising lattices of linear dimensions $L=4,6,8,10,12,14$ and periodic boundary conditions, at a temperature $k_BT/J=2.1$. At this temperature, the correlation length ξ of the infinite system at zero field is already rather small ($\xi \approx 3.7$), and hence the condition $L>\xi$ necessary for the validity of the formulas presented in Sec. II is fulfilled. Since the spontaneous magnetization is already large ($M_{sp}\approx 0.87$), there is a pronounced tendency for metastability of the ordered states, as the minimum of $P_L(s)$ near $s=0$ is already very deep. Hence, rather large observation times are required to sample the thermal equilibrium distribution $P_L(s)$ and the moments $\langle s^k \rangle_L$ correctly. We have obtained satisfactory accuracy for the sizes chosen by usings runs up to about 1.5×10^6 Monte Carlo steps (MCS)/spin.

The susceptibility χ_L has its peak at $H=0$, as expected from Eq. (14); with increasing size the peak height increases dramatically, and at the same time the peaks get much narrower (see Fig. 3). The reduced cumulant U_L [Eq. (19)] is indeed vanishingly small for large H (Fig. 4), then develops a minimum where U_L is negative; for small H it has a sharp peak and clearly converges towards the expected value $U_\infty = \frac{2}{3}$ with increasing system size. The half width at the peaks of the U_L-versus-H curves gives an impression of the accuracy which is reached in the location of the phase boundary: For $L=14$, the half width $\Delta H/J \approx 0.01$; assuming that one can locate the exact position of the peak to an accuracy of $(\frac{1}{5})\Delta H/J$, one would conclude that the phase boundary of the first-order transition between the two states with opposite sign of the magnetization occurs at $H_c/J=\pm 0.002$. With more effort (using, e.g., multispin coding techniques[27] or special purpose processors[26,28]) one clearly could improve this accuracy significantly, but we wish to emphasize that with a rather conventional program (which was used for the studies in Ref. 13 and 14), using standard IBM 3081 computers, one already obtains the accuracy quoted which we consider as rather satisfactory.

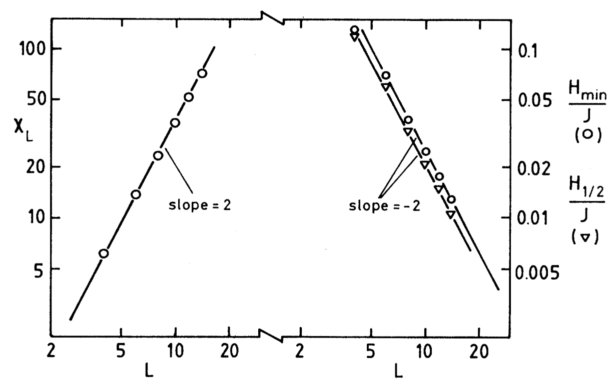

FIG. 5. Log-log plot of susceptibility maximum vs linear dimension (left part) and of characteristic fields vs linear dimension (right part) at $k_BT/J=2.1$. Here H_m denotes the field where the cumulant U_L has its minimum (Fig. 4), while $H_{1/2}$ is the field of the half width of the susceptibility peak.

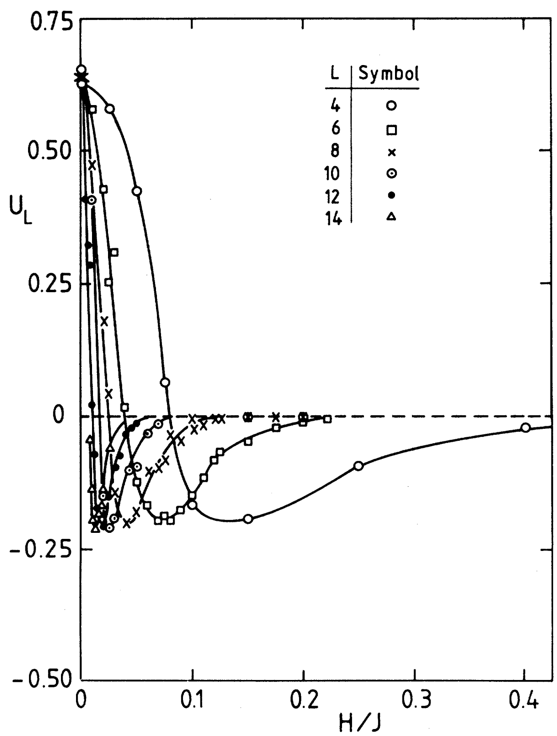

FIG. 4. Reduced cumulant U_L [defined in Eq. (19)] plotted vs magnetic field H at $k_BT/J=2.1$ for various L.

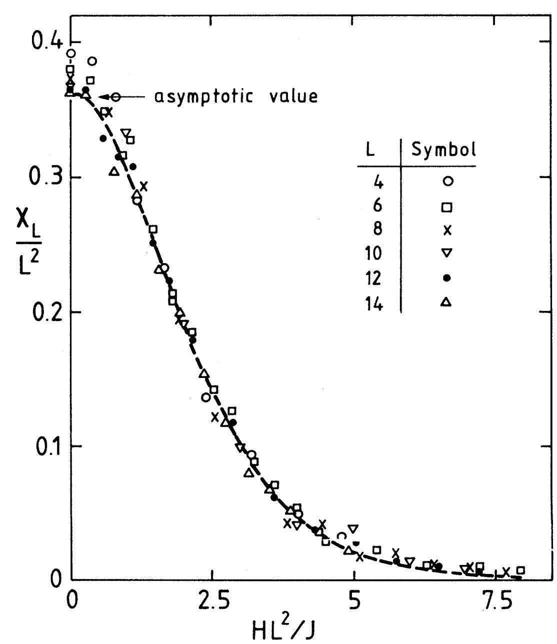

FIG. 6. Scaled susceptibility χ_L/L^2 plotted vs scaled field HL^2/J at $k_BT/J=2.1$ and various L. Arrow indicates the asymptotic value $M_{sp}^2 J/k_BT$ calculated from the exact solution of Yang (Ref. 29).

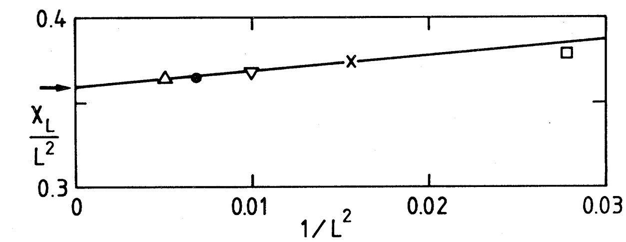

FIG. 7. Scaled susceptibility χ_L/L^2 at $H=0$, $k_BT/J=2.1$ plotted vs $1/L^2$. Arrow indicates the asymptotic value $M_{sp}^2 J/k_BT$ calculated from the exact solution of Yang (Ref. 29).

Next we check the predicted size dependence by plotting the height of the susceptibility maximum as well as various characteristic fields versus system size in log-log form (Fig. 5). These characteristic fields relate to the width ΔH over which the rounding of the first-order phase transition occurs [Eq. (13)]. Indeed the data are nicely consistent with the predictions $\Delta H_{\text{round}} \propto L^{-2}$, and $\chi_L(H=0) \propto L^2$ [Eqs. (13) and (14)].

Moreover, Eq. (14) suggests that χ_L/L^2 can be represented as a single function of a scaled field HL^2/J, apart from a correction term χ/L^2. This means that all the curves of Fig. 3 can be collapsed on a single function. Figure 6 shows that this data collapsing works reasonably well. This is the first time that a scaling function associated with finite-size scaling at a first-order transition has been estimated with Monte Carlo methods.

At small fields one can see systematic deviations from scaling distinctly exceeding the statistical scatter. Figure 7 shows that these deviations are indeed consistent with the variation due to the predicted correction term in Eq. (14), and $\chi_L(H=0)/L^2$ converges to the exactly known value[29] as $L \rightarrow \infty$,

$$\chi_L(H=0)/L^2 = M_{sp}^2/k_BT + \chi/L^2 \ . \tag{20}$$

Thus we conclude that the numerical data conform nicely to the predictions of the phenomenological theory developed in Sec. II, and that finite-size effects at this first-order transition in the Ising model are well understood. Of course, in practice it may be more convenient to observe the metastable hysteresis between $+M_L$ and $-M_L$ (Fig. 1) and extrapolate this behavior to $L \rightarrow \infty$, rather than to apply the present first-principles method, for estimating the spontaneous magnetization; but the present techniques, apart from the fact that its theoretical justification is more satisfactory, may be advantageous in cases where the order of transition is not so clear.

IV. FINITE-SIZE BEHAVIOR OF THE ISING MODEL AT T_c AS A FUNCTION OF THE MAGNETIC FIELD

In order to check whether by this analysis one can clearly distinguish the order of a transition, we have performed precisely the same calculations as above for the critical temperature of the Ising model [$T_c/J \cong 2.269$ (Ref. 30)]. While the qualitative character of the results is

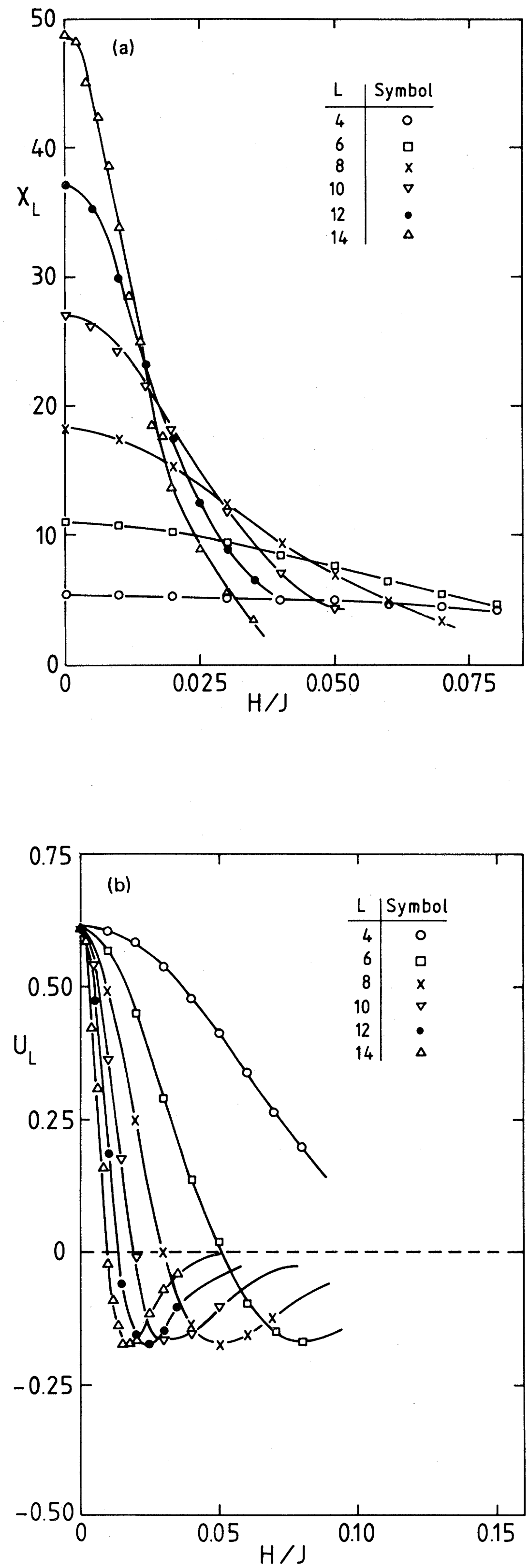

FIG. 8. Susceptibility χ_L (a) and reduced cumulant U_L (b) plotted vs magnetic field at the critical temperature for various L.

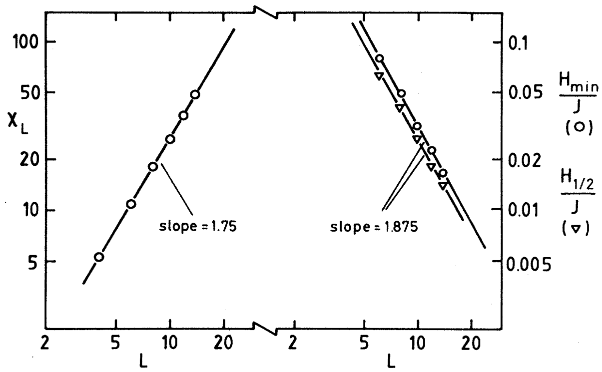

FIG. 9. Log-log plot of susceptibility maximum vs linear dimension (left part) and of characteristic fields (for definitions, see Fig. 5) vs linear dimension (right part) at the critical temperature.

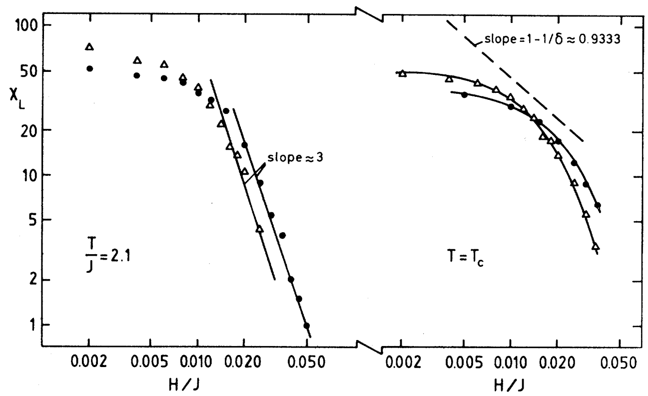

FIG. 11. Log-log plot of the susceptibility vs field at $k_B T/J = 2.1$ (left part) and at the critical temperature (right part), for $L = 12$ (dots) and $L = 14$ (triangles).

the same, one clearly recognizes that the cumulant maximum converges to a distinctly smaller value, $U_L(H=0) \approx 0.618$ in our case (see Fig. 8). This nontrivial cumulant value is the signature of the second-order character of the transition. Above T_c, of course, the distribution tends to a Gaussian and U_L tends to zero.[15]

This conclusion is strongly corroborated when one studies the size dependence of the susceptibility maximum and of the characteristic fields (Fig. 9). Again one finds straight lines, but the slopes are no longer determined simply as the system's dimensionality; rather the slopes reflect the critical exponents γ/ν $(=\frac{7}{4})$ and $(\gamma+\beta)/\nu$ $(=\frac{15}{8})$, since finite-size scaling theory now predicts[1-3]

$$\chi_L = L^{\gamma/\nu} \tilde{\chi}(HL^{-(\gamma+\beta)/\nu}) , \tag{21}$$

where $\tilde{\chi}$ is a nontrivial scaling function. Figure 10 gives direct evidence for this standard form of finite-size scaling. Of course, the fact that such small values of L give a nice fit indicates the fortuitous smallness of all correction terms to finite-size scaling in the Ising model.

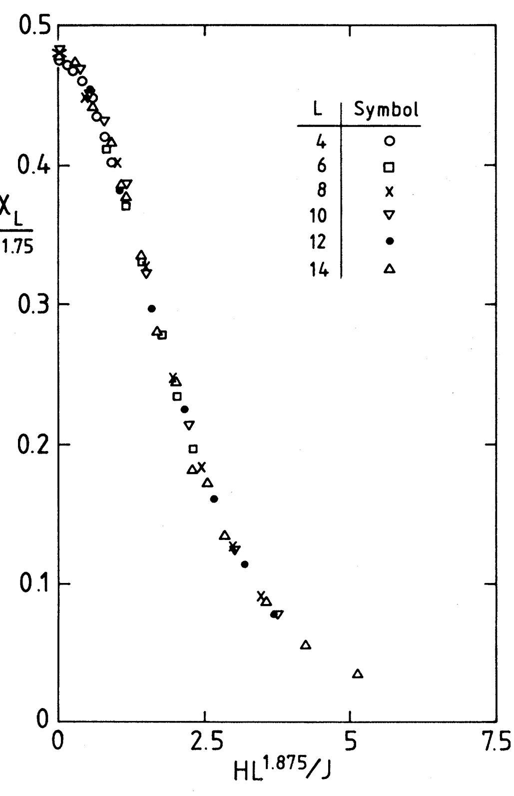

FIG. 10. Scaled susceptibility $\chi_L/L^{1.75}$ plotted vs scaled field $HL^{1.875}/J$ at the critical temperature for various L.

Specific-heat anomalies at phase transitions of monolayers physisorbed on grafoil are typically rounded due to the finite size of the substrate lamellae. Often, it is not clear whether these peaks correspond to rounded second or first-order transitions.[31] Outside the regime of the rounding the specific heat is consistent with a power-law divergence (characteristic of a second-order transition) even in cases where one expects a first-order transition.[31]

This problem has motivated us to present the field dependence of the susceptibility in log-log form (Fig. 11) to check for possible straight-line behavior which can be interpreted in terms of apparent exponents. However, in the present case, the straight-line behavior is restricted to a rather narrow region of fields, and the "exponent" seen is completely unphysical. Even at T_c, where straight-line behavior with slope $1-1/\delta \approx 0.9333$ must occur for $L \to \infty$, this exponent is not seen at all for the present range of sizes and fields. The behavior in Fig. 11 contrasts to the size dependence which gives a much clearer picture (Figs. 5 and 9), but which unfortunately is not accessible experimentally.

V. FINITE-SIZE SCALING AT ASYMMETRIC FIRST-ORDER PHASE TRANSITIONS

Defining a reduced field

$$h = H - H_c(L) , \tag{22}$$

where $H_c(L)$ is an effective critical field where in the finite system the (rounded) transition between both phases occurs, we generalize Eq. (5) as follows:

$$P_L(s)=A\{(2\pi k_B T\chi_+)^{-1/2}\exp\{-[(s-M_+)^2-2\chi_+ sh]L^d/(2k_BT\chi_+)\}$$
$$+(2\pi k_B T\chi_-)^{-1/2}\exp\{-[(s+M_-)^2-2\chi_- sh]L^d/(2k_BT\chi_-)\}\}\ . \tag{23}$$

Here we have assumed a jump of the magnetization from M_+ at $h=0^+$ to $-M_-$ at $h=0^-$ (in the limit $L\to\infty$), and the susceptibilities χ_+ (at $h=0^+$, $s=M_+$) and χ_- (at $h=0^-$, $s=-M_-$) may be different. Of course, the point $s=0$ may be a choice of the origin which need not be of any physical significance; it is the difference $(M_+ + M_-)$ between the two branches which is of physical interest. The constant A is determined by the normalization condition; furthermore, at phase coexistence ($h=0$) it is assumed that the areas under both peaks of the probability distribution are equal.

From the normalization condition, we find instead of Eq. (9)

$$A=L^{d/2}\left[\exp\left[\frac{\chi_+h^2L^d}{2k_BT}\right]\exp\left[\frac{hM_+L^d}{k_BT}\right]+\exp\left[\frac{\chi_-h^2L^d}{2k_BT}\right]\exp\left[-\frac{hM_-L^d}{k_BT}\right]\right]^{-1}\ . \tag{24}$$

With Eqs. (23) and (24) it is a straightforward matter to calculate the moments $\langle s^k\rangle_L$. One obtains

$$\langle s\rangle_L=\frac{(\chi_+h+M_+)\exp\left[\frac{\chi_+h^2L^d}{2k_BT}\right]\exp\left[\frac{hM_+L^d}{k_BT}\right]+(\chi_-h-M_-)\exp\left[\frac{\chi_-h^2L^d}{2k_BT}\right]\exp\left[-\frac{hM_-L^d}{k_BT}\right]}{\exp\left[\frac{\chi_+h^2L^d}{2k_BT}\right]\exp\left[\frac{hM_+L^d}{k_BT}\right]+\exp\left[\frac{\chi_-h^2L^d}{2k_BT}\right]\exp\left[-\frac{hM_-L^d}{k_BT}\right]} \tag{25}$$

and

$$\chi_L=\frac{L^d}{k_BT}(\langle s^2\rangle_L-\langle s\rangle_L^2)$$
$$=\left[[(\chi_+h+M_+)^2+k_BT\chi_+/L^d]\exp\left[\frac{\chi_+h^2L^d}{2k_BT}\right]\exp\left[\frac{hM_+L^d}{k_BT}\right]\right.$$
$$\left.+[(\chi_-h-M_-)^2+k_BT\chi_-/L^d]\exp\left[\frac{\chi_-h^2L^d}{2k_BT}\right]\exp\left[-\frac{hM_-L^d}{k_BT}\right]\right]$$
$$\times\left[\exp\left[\frac{\chi_+h^2L^d}{2k_BT}\right]\exp\left[\frac{hM_+L^d}{k_BT}\right]+\exp\left[\frac{\chi_-h^2L^d}{2k_BT}\right]\exp\left[-\frac{hM_-L^d}{k_BT}\right]\right]^{-1}-\langle s\rangle_L^2L^d/(k_BT)\ . \tag{26}$$

Thus $\langle s\rangle_L$ changes from χ_+h+M_+ for $hM_+L^d\gg k_BT$ to χ_-h-M_+ for $-hM_-L^d\gg k_BT$. The region over which the transition is rounded hence is asymmetric; of course, the exponents governing the size dependence of this width of the rounded region and of χ_L are still given by the dimensionality, as in the symmetric case.

Of course, it is rather straightforward to generalize this treatment to other quantities, such as the internal energy instead of the magnetization; also the intensive variable driving the transition may be the temperature itself; rather than a field. Then χ_+, χ_- in the above formulas get the meaning of specific heats at phase coexistence.

VI. CONCLUSIONS

In the present work, we have analyzed finite-size effects at first-order phase transitions based on thermodynamic fluctuation theory. This treatment agrees with corresponding renormalization-group work, which has predicted that the transition is smeared over a region of order L^{-d}, and that the δ-function singularity is replaced by a peak of height proportional to L^d; moreover, our treatment yields explicit predictions for the finite-size scaling functions describing these smeared-out singularities.

As an application, the phase transition of the square Ising model below T_c as a function of magnetic field is considered. We find good agreement with the theoretial predictions with a still moderate computing effort; it is also not difficult to distinguish the behavior from the finite-size rounding at the second-order transition at T_c in this case. Thus we think that the present considerations should be useful for the analysis of finite-size effects at other first-order transitions, seen in either computer simulations or experiments.

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[1]M. E. Fisher, in *Critical Phenomena,* edited by M. S. Green (Academic, New York, 1971), p. 1.

[2]M. E. Fisher and M. N. Barber, Phys. Rev. Lett. **28**, 1516 (1972).

[3]M. P. Nightingale, J. Appl. Phys. **53**, 7927 (1982).

[4]M. N. Barber, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic, New York, 1983), Vol. 8, p. 145; see also K. Binder, *ibid*, Vol. 8, p. 1.

[5]Y. Imry, Phys. Rev. B **21**, 2042 (1980).

[6]M. E. Fisher and A. N. Berker, Phys. Rev. B **26**, 2507 (1982).

[7]H. W. J. Blöte and M. N. Nightingale, Physica **112A**, 405 (1982).

[8]P. Kleban and C.-K. Hu (unpublished).

[9]J. L. Cardy and M. P. Nightingale, Phys. Rev. B **27**, 4251 (1983).

[10]V. Privman and M. E. Fisher, J. Stat. Phys. **33**, 385 (1983).

[11]K. Binder, Thin Solid Films **20**, 637 (1974).

[12]K. Binder, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and M. S. Green (Academic, New York, 1976), Vol. 5B, p. 1.

[13]D. P. Landau, Phys. Rev. B **13**, 2997 (1976); **14**, 225 (1976).

[14]K. Binder and D. P. Landau, Phys. Rev. B **21**, 1941 (1980); D. P. Landau and K. Binder (unpublished).

[15]K. Binder, Phys. Rev. Lett. **47**, 693 (1981); Z. Phys. B **43**, 119 (1981).

[16]For reviews see, D. P. Landau, in *Monte Carlo Methods in Statistical Physics,* edited by K. Binder (Springer, Berlin, 1979); p. 121; K. Binder, *ibid*, p. 1; D. P. Landau, in *Applications of Monte Carlo Methods in Statistical Physics,* edited by K. Binder (Springer, Berlin, 1984), p. 93; K. Binder and D. Stauffer, *ibid*, p. 1.

[17]D. P. Landau and K. Binder, Phys. Rev. B **17**, 2328 (1978).

[18]K. Binder, Z. Phys. B **45**, 61 (1981); T. L. Polgreen, Phys. Rev. B **29**, 1468 (1984).

[19]K. Binder, J. Stat. Phys. **24**, 54 (1981); H. J. Herrmann, Z. Phys. B **35**, 171 (1979).

[20]D. P. Landau and R. J. Swendsen, Phys. Rev. Lett. **46**, 1437 (1981).

[21]A preliminary account of this discussion has already been reviewed by K. Binder and D. Stauffer in Ref. 16.

[22]R. J. Glauber, J. Math. Phys. **4**, 263 (1963).

[23]J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena,* Ref. 4, Vol. 8, p. 269.

[24]For somewhat related work, see also L. S. Schulman, J. Phys. A **13**, 237 (1980); A. D. Bruce, T. Schneider, and E. Stoll, Phys. Rev. Lett. **43**, 1284 (1979); A. D. Bruce, J. Phys. C **14**, 3667 (1981); and Refs. 5 and 10.

[25]J. M. J. van Leeuwen, Phys. Rev. Lett. **34**, 1956 (1975); B. Nienhuis and M. Nauenberg, *ibid*. **35**, 477 (1975).

[26]M. N. Barber, R. B. Pearson, D. Toussaint, and J. L. Richardson (unpublished).

[27]L. Jacobs and C. Rebbi, J. Comput. Phys. **41**, 203 (1981); R. Zorn, H. J. Herrmann, and C. Rebbi, Comput. Phys. Commun. **23**, 337 (1981).

[28]R. B. Pearson, J. L. Richardson, and D. Toussaint, J. Comput. Phys. **51**, 243 (1983); A. Hooghland, J. Spaa, B. Selman, and A. Compagner, *ibid*. **51**, 250 (1983).

[29]C. N. Yang, Phys. Rev. **87**, 410 (1952).

[30]L. Onsager, Phys. Rev. **65**, 117 (1944).

[31]R. Marx and E. F. Wassermann, Surf. Sci. **117**, 267 (1982).