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Absence of enhanced fluctuations as a first-order phase transition is approached: An exact transfer-matrix study

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As a second-order phase transition is traversed critical scattering appears; these fluctuations serve notice of the impending loss of stability of the equilibrium phase. For a model first-order phase transition we *rigorously* prove, using *exact* thermodynamic quantities obtained from strip-transfer-matrix calculations, as well as finite-size-scaling analysis, that as a temperature-driven, symmetry-breaking, first-order phase transition is approached, no *enhancement* of fluctuations into the future product phase occurs. To be specific, we study the probability of occupation of the product phase (stable below the transition temperature), and demonstrate that this is a monotonically decreasing function as the transition temperature is approached from above. The relation of this pedagogical result to x-ray scattering experiments is discussed.

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I. INTRODUCTION

The exact analytical solution to the two-dimensional (2D) Ising model [1] has provided a valuable guide to the properties of second-order phase transitions. In particular, it is known that the magnetic susceptibility diverges to infinity at the critical temperature [2], and via the fluctuation-dissipation theorem we thus know that critical scattering will also occur as the transition is approached. There are many experimental verifications of this behavior in magnetic systems as well as in structural phase transitions [3] (apart from the central-peak phenomenon [4], which may be explained via defects [5]).

In first-order phase transitions the situation is different. To be specific, the natural question concerning the analog of critical fluctuations is as follows: As a first-order phase transition is approached, does the impending loss of thermodynamic stability of a given phase manifest itself in the form of enhanced fluctuations into the product phase? In this Brief Report we shall use exact thermodynamics to rigorously prove that for our model system the correct answer is no, in agreement with a very old conjecture made by Fisher [6]. While this result cannot be considered to be new, our pedagogical analysis of the probability of the ensuing product phase is instructive, and we show how our work allows for direct comparison with some experimentally observed quantities.

Many experiments studying this question have concentrated on displacive structural phase transitions, including so-called martensitic phase transitions. For pure systems, such as the alkali metals [7] and the group-III*a* and -IV*a* metals [8], it is clear that no indications of such heterophase fluctuations into the product phase are found in inelastic-neutron-scattering studies. Alternatively, in impure systems [9], it is clear that such fluctuations do occur, and even static domains of the product phase are seen coexisting with the host matrix. Experiments on other types of systems have been extensively reviewed by Yukalov [10].

We shall focus on a simple model that can be interpreted to represent a structural phase transition, although its application is much more general. We consider a 2D square lattice, where at each lattice site a single scalar degree of freedom is present. Denoting the scalar at a

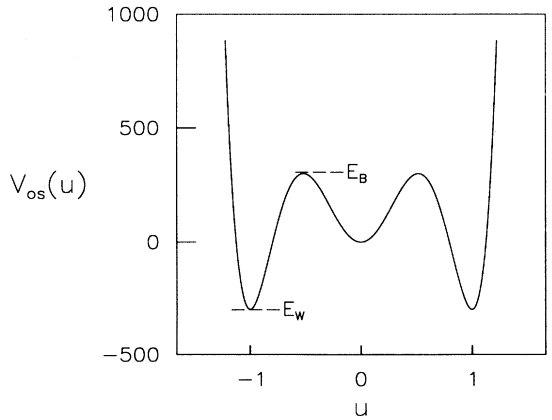

FIG. 1. The on-site potential V_{OS} given in Eq. (1) that acts upon the single component scalar degree of freedom present at each site. One may scale the potential such that u_0 takes on any value (here it is chosen to be 1), and then only the energy barrier E_B and the ratio of the barrier to the energy well depth E_B/E_W need to be specified.

chosen site by u, we specify that the local potential be given by

$$V_{\rm OS}(u)=\tfrac{1}{2}au^2-\tfrac{1}{4}bu^4+\tfrac{1}{6}cu^6 . \quad (1)$$

This so-called ϕ^6 potential, for appropriately chosen a, b, and c (which we stress are temperature independent), is shown in Fig. 1. This potential corresponds to two stable states of $u=\pm u_0$, as well as one metastable state at $u=0$; note that $V_{\rm OS}(u)=V_{\rm OS}(-u)$. Then, every site is coupled to its near neighbors by an interaction (which we specify below) such that the ground state corresponds to a symmetry-broken state with the same value of $u=u_0$ or $u=-u_0$ being assumed on every site. At very high temperatures it is clear that the "particles" will not be localized in any of the wells of $V_{\rm OS}$, but rather the thermal expectation value of u, denoted by $\langle u \rangle$, will be zero. Due to the energy barriers E_B shown in Fig. 1, it is clear that a first-order phase transition will occur at some intermediate temperature T_1 where $\langle u \rangle$ jumps from zero to a value close to $\pm u_0$.

We now specify the interparticle interaction potential. In analogy with ϕ^4 classical field theory, it is clear that the simplest model of a temperature-driven, symmetry-breaking, first-order phase transition may be constructed using $V_{\rm OS}$ and an intersite coupling potential which is simply harmonic, viz.,

$$V_{\rm IS}(\{u_i\})=\frac{k}{2}\sum_{(i,j)}(u_i-u_j)^2 , \quad (2)$$

where the lattice sites of our 2D net are denoted by i, and near neighbors are specified by (i,j). However, as has been discussed elsewhere [11], the driving force for this model is a configurational entropy of ln(2) per site, and thus leads to a very weak transition. By taking note of a continuum field theory of this system that involves higher-order couplings, viz.,

$$H_{\rm eff}=\int d^2\mathbf{r}\left[V_{\rm OS}(u)+\frac{k}{2}(\nabla u)^2+\frac{\alpha}{2}u^2(\nabla u)^2+\cdots\right], \quad (3)$$

it was recognized [12] that the driving force of this system can be changed to an arbitrarily large amount of vibrational entropy if the following (again, temperature-independent) Hamiltonian is considered:

$$H=\sum_i V_{\rm OS}(u_i)+V_{\rm IS}+\sum_{(i,j)}\frac{\alpha}{4}(u_i^2+u_j^2)(u_i-u_j)^2 . \quad (4)$$

We have previously demonstrated that this latter term allows this system to approach its bulk limit very rapidly [11,13], and this is explained below.

II. FINITE-SIZE-SCALING FORMALISM

Our work shall employ the transfer-matrix technique; this allows for the *exact* determination of the equilibrium thermodynamics of a system. This is to be contrasted with the Monte Carlo technique, which when applied to first-order phase transitions must overcome the large energy barriers at strongly first-order phase transitions by approximating ergodic trajectories with very long simulations.

We shall consider a 2D lattice that is infinite in extent in one dimension only, and of breadth L in the other. This will allow strip-transfer-matrix calculations to be done [14]; bulk thermodynamic quantities are then found by implementing finite-size scaling appropriate to this geometry. Previously, we have presented an exhaustive study of our finite-size-scaling ansatz for temperature-driven, symmetry-breaking, first-order phase transitions [13] for systems of this geometry. Here we simply note that the scaling form for the singular part of the reduced Gibb's free energy is

$$g_s=\frac{A}{L\xi}W_T(t\Delta SL\xi) , \qquad t=\frac{T-T_1(L)}{T_1(L)} , \quad (5)$$

where W_T is a universal function. In Eq. (5), $T_1(L)$ is the analog of the transition temperature for a finite L (which may conveniently be defined as the temperature at which the specific heat peaks), ξ corresponds to the domain-wall separation of the low-temperature variants (technically, this is the most slowly diverging transfer-matrix correlation length), and ΔS is the change of entropy occurring at the transition [13]. The physics behind Eq. (5) is clear—the driving force for a temperature-driven transition is the entropy, and thus the argument of the universal function W_T is simply the reduced latent heat $t\Delta S$ multiplied by the average area of a domain of the low-temperature product phase. In the bulk limit, since the free energy per particle is intensive, $W_T(y)\propto|y|$. Then, from Eq. (5) it follows that for a finite value of L the transition region will not contain a cusp in the Gibb's free energy, but instead will be rounded over a temperature interval (that is, of course, dependent upon L) defined by

$$\Delta T(L)\sim\frac{T_1(L)}{\Delta SL\xi} . \quad (6)$$

The transfer-matrix correlation length ξ diverges like $\exp(L)$, and one then finds [11,13] the very desirable result (for practical numerical studies) that the finite-size-affected regime defined by Eq. (6) vanishes very rapidly with L.

With the scaling form of the free energy given in Eq. (5) combined with the above definition of the finite-size-affected regime, one may scale the argument of a given thermodynamic function such that it is independent of L (providing the system is large enough) by replacing the argument by

$$y=\frac{T-T_1(L)}{\Delta T(L)} . \quad (7)$$

A verification of this scaling form is provided in Ref. [13] (in particular, see Fig. 7). Finally, the relevance of the nonlinear, intersite coupling term (α) in Eq. (4) may be shown to be the amazing reduction of $\Delta T(L)$ by many orders of magnitude, even for a 1D system [11,13].

Recently, another finite-size-scaling study of temperature-driven, symmetry-breaking, first-order phase transitions has been given by Lee and Kosterlitz [15]. The aim of their work was similar to that of our Ref. [13], viz., the prediction of bulk equilibrium thermodynamic quantities. In particular, their theory has been developed to account for finite-size effects in d-dimensional hypercubic systems. Thus, similar to work on the first-order field-driven transition in the $d=2$ Ising

model for $T < T_c$ [16], these two finite-size-scaling theories may be implemented depending on which geometry is being used. However, it should be stressed that the approach to the thermodynamic limit goes as an inverse power law for hypercubic systems, whereas from Ref. [13] it follows that the approach is exponentially fast, and as mentioned above, this allows for a more practical numerical search of the region close to the thermodynamic limit.

III. STUDY OF PRODUCT PHASE OCCUPATION ABOVE T_1

For convenience only, we discretize the scalar u at each site such that it only takes on the five values $u = 0, \pm u_0/2, \pm u_0$. Then in Fig. 2 we show the entropy of this system as a function of the scaled parameter y for $L = 1,2,3,4,5,6$. Note that $\Delta T(L=1) = 483$, and $\Delta T(L=6) = 0.38$; clearly, as L increases these systems are rapidly approaching the bulk limit. The importance of Fig. 2 is in the verification that our system is indeed undergoing a first-order transition, as the developing discontinuity in the entropy is associated with the latent heat. Further, it demonstrates that except for the temperature range $T_1 - \Delta T(L) \rightarrow T_1 + \Delta T(L)$, which is very small for $L = 6$, this system is behaving as would its bulk limit counterpart.

We now specify our view of enhanced fluctuations at a temperature-driven, symmetry-breaking, first-order phase transition, using the above Hamiltonian as a simple example system. We wish to stress that the *entire* point of this exercise is to make and demonstrate our precise definition of enhanced fluctuations utilizing exact thermodynamics; *no* conclusions concerning the dynamics are possible via equilibrium statistical mechanics—thus we must be content with making statements on static equilibrium quantities. Here, we focus on the probability distribution function, $P(u)$. Let T_1 be approached from above. Quantify the portion of time the system spends in either of the side wells by $P(u = \pm u_0) \equiv P_{\text{side}}$, and then examine how this quantity varies with temperature. We define enhanced fluctuations (inappropriately named heterophase fluctuations for systems in true equilibrium [10]) as a temperature range just above T_1 where $\partial P_{\text{side}}/\partial T < 0$. To be specific, if this inequality is satisfied, then as the transition is approached from above, the system will tend to start to display its later tendency (viz., at lower temperatures) to transform into a side well state. If this does not occur until the temperature is precisely equal to T_1, then one may say that the system behaved as if it was completely unaffected by the impending transition; instead, the side wells may be viewed as excited states of the $\langle u \rangle = 0$ phase, and as the temperature is lowered the occupation of these excited states simply decreases. Clearly, the latter behavior is in sharp contrast to the presence of critical fluctuations found at second-order phase transitions.

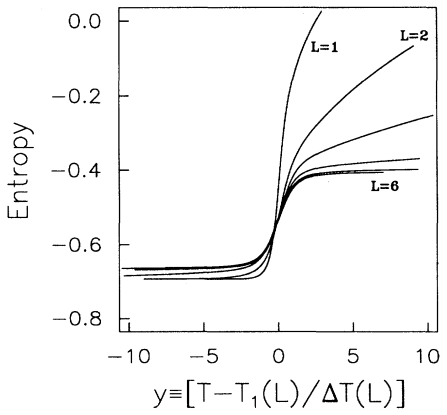

FIG. 2. The entropy vs the scaled temperature variable y for $L = 1,2,3,4,5,6$. We have specified the Hamiltonian's parameters using the following values: $E_B = 300$, $E_B/E_W = 1$, and $k = \alpha = 40\,000$ (see Ref. [13] for more thermodynamic data for this system).

For the above model it is clear that if we wish to apply this definition we require knowledge of $P(\pm u_0)$, the equilibrium probability distribution function for u at any one site, evaluated for one of the side well states; this is an easy quantity to calculate within transfer matrix calculations [13], being a function of ϕ_0, the transfer matrix eigenvector of the largest eigenvalue. In Fig. 3 we plot this quantity for temperatures above T_1. We focus on the temperature at which the minimum occurs for each L, denoted by $T_{\min}(L)$. In this figure the position of the minima clearly decreases linearly with L for $L > 1$. As demonstrated above and elsewhere [13], for this model we are in the scaling regime for $L > 2$, and thus we are guaranteed that this behavior will continue in the limit $L \rightarrow \infty$.

If we denote the position of the minima by $T_{\min}(L)$, then this linear behavior implies that

$$T_{\min}(L) - T_1(L) \propto \exp[-CL] , \tag{8}$$

suggesting that the positions of the minima vanish *exponentially fast* as the bulk limit is approached. We have fit the positions of the minima for $L \geq 3$ to the form

$$T_{\min}(L) - T_1(L) = T_0 + A \exp[-CL] . \tag{9}$$

The best fit corresponds to a T_0 that is slightly negative,

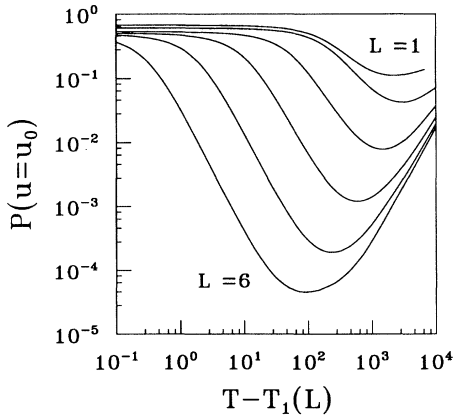

FIG. 3. The probability distribution function $P(\pm u_0)$ vs $T - T_1(L)$. The quantity $T_{\min}(L)$ is defined to be the minimum value of $P(\pm u_0)$ for $T > T_1(L)$.

which is clearly unphysical—thus the only physically reasonable fit is with $T_0=0$. Also, assuming that $T_0=0$, the fit is excellent. Clearly, our exact thermodynamics shows that $T_{\min}$ has as its asymptotic value T_1 in the 2D limit. Thus according to our above definition we see that there are no enhanced fluctuations into the ensuing product state as the temperature is lowered towards T_1 for the bulk system.

IV. DISCUSSION

In this paper we have used exact thermodynamic quantities extracted from transfer-matrix calculations, and our finite-size-scaling theory, to analyze the probability distribution function of the product phase (stable below T_1) as T_1 is approached from above. Consequently, we were able to invent a definition of "enhanced fluctuations as the phase transition is approached," viz., $\partial P_{\text{product}}/\partial T<0$, which we showed did not occur in our model system in the bulk limit as T_1 was approached from above. Here we briefly comment on the relevance of this result to experimentally accessible quantities.

It seems that local probes, similar to the EPR [17] studies of second-order transitions, may be best suited to study this issue when applied to structural phase transitions; quite simply, the consequences of the relation expressed in Eq. (8) refer to the probability distribution function for a single site. In contrast to this, it is very difficult to relate our work to the standard experimental probe of reciprocal space, viz., neutron scattering, that has been used in characterizing the martensitic phase transitions that motivated our work. Unfortunately, equilibrium statistical mechanics does not allow for statements concerning the dynamics structure factor, viz., $S(\mathbf{q},\omega)$, to be made, and thus for both of these experiments we cannot directly relate our result to observables.

The structure factor probed in x-ray work, $S(\mathbf{q})$, can be accessed through transfer-matrix calculations; however, the knowledge of all eigenvalues of the transfer matrix is required [11]. Further, the model discussed here involves a transition between two $\mathbf{q}=\mathbf{0}$ states. It is possible to produce a model, similar to that given in Eq. (4), where the transition is to a $\mathbf{q}=(\pm\pi,\pm\pi)$ state, and then the instantaneous correlations provided by this measurement may be understood in terms of exact thermodynamic quantities; this work will be reported elsewhere [18]. Given that $S(\mathbf{q})$ measures instantaneous correlations in a system, our result *will* arise as the lack of enhancement of $S(\mathbf{q}_0)$ as T_1 is approached from above, where $\mathbf{q}_0$ is the wave vector of the low-temperature product phase.

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[1] L. Onsager, Phys. Rev. **65**, 117 (1944).
[2] B. McCoy and T. T. Wu, *The Two-Dimensional Ising Model* (Harvard, Cambridge, 1973).
[3] A. D. Bruce and R. A. Cowley, *Structural Phase Transitions* (Taylor-Francis, London, 1981).
[4] S. M. Shapiro *et al.*, Phys. Rev. B **6**, 4332 (1972).
[5] B. I. Halperin and C. M. Varma, Phys. Rev. B **14**, 4030 (1976).
[6] M. E. Fisher, Physics **3**, 255 (1967).
[7] H. A. Smith *et al.* (unpublished).
[8] W. Petry, T. Flottmann, A. Heiming, J. Trampenau, M. Alba, and G. Vogl, Phys. Rev. Lett. **61**, 722 (1988); W. Petry, A. Heiming, J. Trampenau, M. Alba, C. Herzig, H. R. Schober, and G. Vogl, Phys. Rev. B **43**, 10933 (1991); A. Heiming, W. Petry, J. Trampenau, M. Alba, C. Herzig, H. R. Schober, and G. Vogl, *ibid.* **43**, 10948 (1991); J. Trampenau, A. Heiming, W. Petry, M. Alba, C. Herzig, W. Miekeley, and H. R. Schober, *ibid.* **43**, 10963 (1991).
[9] S. M. Shapiro, B. X. Yang, Y. Noda, L. E. Tanner, and D. Schryvers, Phys. Rev. B **44**, 9301 (1991).
[10] V. I. Yukalov, Phys. Rep. **208**, 395 (1991).
[11] J. R. Morris and R. J. Gooding, Phys. Rev. Lett. **65**, 1769 (1990); Phys. Rev. B **43**, 6057 (1991).
[12] R. J. Gooding, Scr. Metall. **25**, 105 (1991).
[13] J. R. Morris and R. J. Gooding, J. Stat. Phys. **67**, 471 (1992).
[14] M. P. Nightingale, in *Finite-Size Scaling and Numerical Simulation of Statistical Systems,* edited by V. Privman (World Scientific, Singapore, 1990).
[15] J. Lee and J. M. Kosterlitz, Phys. Rev. B **43**, 3265 (1991).
[16] V. Privman and M. E. Fisher, J. Stat. Phys. **33**, 385 (1983).
[17] K. A. Mueller, in *Nonlinear Phenomena at Phase Transitions and Instabilities,* edited by T. Riste (Plenum, New York, 1981).
[18] J. H. Yao and R. J. Gooding (unpublished).