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Evidence for Spinodal Singularities in High-Dimensional Nearest-Neighbor Ising Models

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Conventional theories of nucleation predict that the metastable state has an average lifetime which monotonically decreases as the system is quenched further from the condensation point. However, theories based on the coarse-grained Ginzburg–Landau free energy functional seem to indicate that for systems above six dimensions there is a sharp spinodal dividing the metastable and unstable regimes where the lifetime of the metastable state diverges. Monte Carlo simulations are used to investigate this discrepency. Both nucleation rates and bulk susceptibility measurements seem to support the prediction of the Ginzburg–Landau theories.

KEY WORDS: Nucleation; spinodal; metastability; mean-field; Monte Carlo; Ising model.

1. INTRODUCTION

In the theory of first-order phase transitions, it is well known that mean-field approximations exhibit a sharp boundary between the metastable and unstable regimes.[1] This is commonly referred to as the *spinodal* or *limit of metastability*. Although the spinodal is well defined in mean-field approximations, it is not observed in more realistic systems with short-range forces.[2] Instead, one finds a region of smooth crossover from metastable to unstable behavior in which the initially metastable system decays to equilibrium via the formation of nucleating droplets.[1] As the system is quenched closer to the unstable regime, nucleating droplets occur with greater frequency and the lifetime of the metastable state decreases monotonically.

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In spite of the success of the above picture, there have been several hints in theoretical studies of metastable Ising models which suggest that the behavior is different in systems where the dimension of space d is greater than six. A cursory glance at the results seems to indicate that the lifetime of the metastable state in fact *diverges* at a well-defined spinodal. For example, in a renormalization group analysis of Ginzburg–Landau models with uniform field densities, Gunton and Yalabik discovered a fixed point representing the spinodal.[3] Their calculation showed that the fixed point was stable above six dimensions even under perturbations which introduced a small gradient term. The small spatial variations should have allowed nucleating droplets to form which would have destroyed the stability of the system.

In addition, the work of Klein and Unger concerning the effect of the spinodal in long-range Ising models resulted in a scaling form for the nucleation barrier ΔF which diverged at the spinodal above six dimensions[4]:

$$\Delta F \sim R^d (\Delta H)^{3/2 - d/4} \tag{1}$$

Here, ΔH is the reduced distance to the spinodal value of the external field at constant temperature and R is the range of interaction between spins.

To date, these anomalous results have largely been ignored. This is not too surprising, since the divergence of the lifetime of the metastable state with quench depth is a feature which is not observed in standard phenomenological nucleation theories. However, the theories based on the coarse-grained Ginzburg–Landau free energy functional seem to give the correct predictions in the case of Ising models with long-range interactions.[5–7] It is the purpose of the present work to determine whether or not a spinodal singularity appears in nearest-neighbor Ising models above six dimensions.

This problem is approached in two different ways. First, nucleation rates are measured and compared to the theoretical values predicted by the classical nucleation theory (CNT) of Becker and Döring[1] for $d=5$ and $d=7$ systems. Next, the behavior of the magnetic susceptibility in the metastable state (i.e., the quasistatic susceptibility) is investigated and compared to the results from a Curie–Weiss model.[8]

2. METHODS

The Ising models in the simulations are governed by the usual Hamiltonian:

$$\mathscr{H} = -\mathscr{J} \sum_{\langle ij \rangle} s_i s_j - H \sum_i s_i \tag{2}$$

The first sum is over all nearest-neighbor pairs of spins and the coupling constant $\mathcal{J}$ is positive, so that the system is ferromagnetic. In the second sum, H is the constant, external field which couples to all spins.

The simulations employ Glauber dynamics (Model A in the categorization of Hohenberg and Halperin[9]), using the standard Metropolis heat-bath algorithm.[10] Every spin in the system is tested for flipping once per Monte Carlo step. The temperature is set to $-0.55T_c$ and helical boundary conditions are used. There was no appreciable difference observed between the behavior of simulations with helical boundary conditions and those with periodic boundary conditions which were employed in a preliminary study at Boston University.

Initially, the system is configured so that all spins are pointing antiparallel to the external field. Under the heat-bath dynamics, the system can then relax into a metastable state where the majority of spins remain antiparallel to the field. If H is too large, the system is unstable and no evidence of a metastable state is observed.

The shorter simulations were run on SUN4 workstations and on a Hewlett-Packard mainframe. Longer simulations were run on a Cray-YMP and were vectorized according to the "checkerboard" algorithm[11] which is a standard method used for vectorization of nearest-neighbor Ising models.

3. NUCLEATION RATES

A test for the existence of spinodal singularities can be performed through the measurement of nucleation rates. In general, a metastable system is observed to decay to equilibrium by means of the formation of local regions of the stable phase. Random fluctuations cause these centers or *droplets* to form according to a certain size distribution. When a droplet greater than some critical size occurs, it rapidly grows in a radial fashion and takes the whole system to equilibrium. These are called *nucleating droplets*. The number of nucleating droplets which form per unit time per unit volume is called the *nucleation rate*.

In the limit of small external field, the nucleation rates are found to be accurately described by the phenomenological theory of Becker and Döring.[1] According to this theory, the nucleation rate J is given by the following expression:

$$J = P_k P_s e^{-c/h^{(d-1)}} \tag{3}$$

The variable c depends upon the dimension of space, the surface tension, and the temperature. It is independent of the external field. The prefactors of the exponential are defined according to their dependence upon the details of the dynamics. P_s is a function only of the equilibrium properties of the system. P_k is a function which depends upon the dynamics used in the simulation.

When the external field is small, the exponential in Eq. (3) dominates the behavior of the nucleation rate. Since the theory is valid in the limit of small field, this is the regime of interest. When the log of the nucleation rate is plotted as a function of $1/h^{(d-1)}$, it should behave linearly with a negative slope having magnitude c. This is considered to be the hallmark of classical nucleation theory.

Given the value of the bulk surface tension, c may be calculated. It is difficult to obtain accurately a value for the surface tension in high dimensions. However, the value of the surface tension in the limit where the temperature goes to zero is known to be equal to $2\mathscr{J}$ per unit surface area in all dimensions. As the temperature increases, the surface tension monotonically decreases and goes to zero at the critical point. The $T=0$ value of the surface tension can be used to calculate an upper bound for c, and this is the approach used in the present work.

Another difficulty encountered when attempting to measure nucleation rates in high dimensions is the identification of nucleating droplets. It is time consuming to search for droplets every Monte Carlo step. Because of this problem, a different criterion for J was chosen. The simulations were run until the magnetization changed sign. This means that at least one nucleating droplet had formed and grown to a mass containing more than half of the spins in the system. After taking an average of several of these times, the nucleation rate was defined to be the inverse of the average time for the magnetization to flip divided by the volume of the system.

The criterion is not good for cases where more than one droplet forms during the course of the simulation. It is also bad when the time for the subsequent growth of the nucleating droplet is longer than or comparable to the average time of formation. However, both of these situations occur when the external field is relatively large and the system is not in the CNT regime. For small nucleation rates the criterion is assumed to be adequate.

Figure 1 shows a semilog plot of the nucleation rate versus $1/h^{(d-1)}$ for $d=5$ for several different system sizes. The larger systems show two distinct regimes. On the left-hand side of the plot the curves are relatively flat. This is where the external field is large and should correspond to the regime where the system has no clearly definable metastable state. Instead, it is unstable and quickly decays to equilibrium in a certain number of Monte Carlo steps which is insensitive to the value of the external field.

On the right-hand side of Fig. 1, the large systems exhibit a second type of behavior. This is presumed to be the regime governed by CNT. The time for the formation of droplets is very long and J is independent of

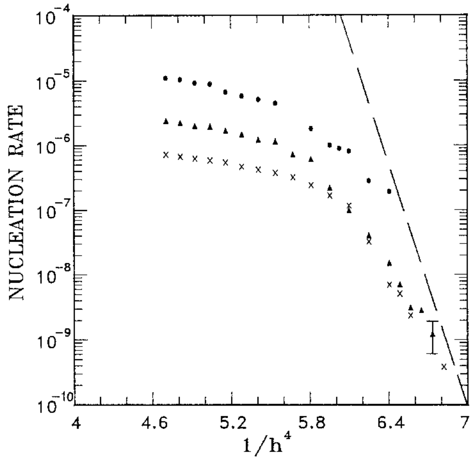

Fig. 1. Nucleation rates for $d = 5$ Ising models. Bullets, triangles, and crosses indicate system sizes of $L = 5$, 7, and 9, respectively. The dashed line gives the maximum slope predicted by classical nucleation theory.

system size. Indicated in the plot is the maximum CNT slope, which uses the $T = 0$ surface tension (a smaller value of the surface tension would give a smaller slope). The temperature is approximately $0.55T_c$. If, as in two and three dimensions, the surface tension has decreased by 5%, the theoretical slope should be about 3/4 of the maximum. This appears to be roughly true in this case.

Figure 2 shows the nucleation data for the $d = 7$ simulations. As in the

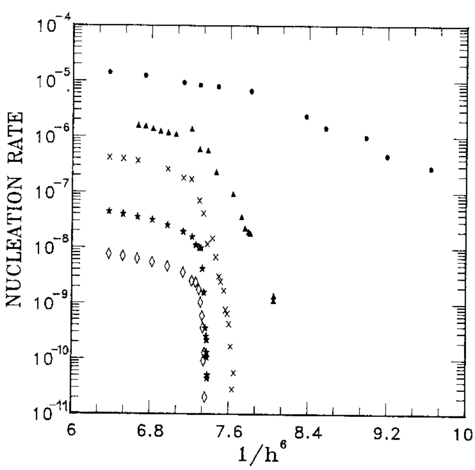

Fig. 2. Nucleation rates for $d = 7$ Ising models. Bullets, triangles, crosses, stars, and diamonds indicate system sizes of $L = 3$, 4, 5, 7, and 9, respectively.

$d=5$ plots, the large systems exhibit two regimes. The left-hand side appears to be the unstable regime where the nucleation rate does not depend strongly upon the external field. The right-hand side should be governed by the exponential factor in Eq. (4) which is predicted by CNT.

Since the $d=7$ nucleation data fall off so sharply in large systems, it is instructive to look at the data with an expanded abscissa. Figure 3 shows the data in the region where the $L=7$ and $L=9$ plots exhibit the presumed CNT behavior. A maximum bound on the slope calculated using the $T=0$ surface tension is also shown. Both the $L=7$ and the $L=9$ data seem to have slopes which are greater than the maximum CNT bound. If the surface tension is assumed to be 5% less than the $T=0$ value, the theoretical slope should be roughly 2/3 that of the pictured slope and thus in even stronger disagreement with the data!

In order for the J values to behave according to CNT at small values of the external field, something remarkable must happen in the plots at lower nucleation rates. For example, the loci could continue their steep descent and then deviate to the smaller CNT slope. This would indicate the presence of another time scale in the problem. Although a possibility, the author does not know of any physical reason for this type of behavior to occur. Another explanation is that there is actually a spinodal singularity in the $d=7$ system. In the limit where the size of the system becomes infinite, the observed steep dropoff would approach a step function as in the case of an infinite-range mean-field system. The location of the step would be the sharp spinodal line.

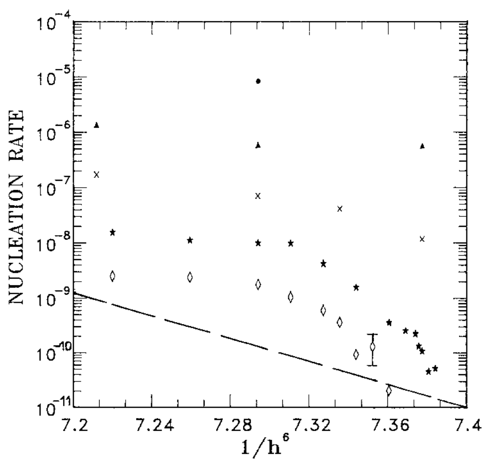

Fig. 3. Expanded view of $d=7$ nucleation rates from Fig. 2 in the regime where the $L=7$ and $L=9$ data drop sharply. The dashed line gives the maximum slope predicted by classical nucleation theory.

4. QUASISTATIC SUSCEPTIBILITY

The *quasistatic susceptibility* is defined as the fluctuations in the magnetization while the system remains metastable:

$$\chi_{qs} = N(\langle m^2 \rangle_{ms} - \langle m \rangle_{ms}^2) \tag{4}$$

Here, N is the number of spins in the system and m is the magnetization per spin. The brackets $\langle \cdot \rangle_{ms}$ indicate an average over metastable configurations. It is a restricted average, since configurations near equilibrium are excluded. Although this type of average is difficult to define mathematically, it is a physically valid operation. In both experimental systems and in simulations, metastable states are commonly observed where the lifetime is found to be very large with respect to all other relevant time scales.

In Fig. 4, the quasistatic susceptibility is plotted versus the magnetic field H for five-, six-, and seven-dimensional metastable nearest-neighbor Ising models. Each point was taken from averages of three runs of 4000 Monte Carlo steps per spin. If the system decayed during this time, no data were recorded.

Qualitatively in five and six dimensions, χ_{qs} increases slightly as H is increased and the system is quenched deeper into the metastable regime. The curves end where the quasistatic susceptibility can no longer be defined because the systems do not remain metastable for the duration of the simulation. It might be possible to try to measure critical exponents based on an extrapolation of these "pseudospinodal" curves, but there does not appear to be any real divergence of χ_{qs}.

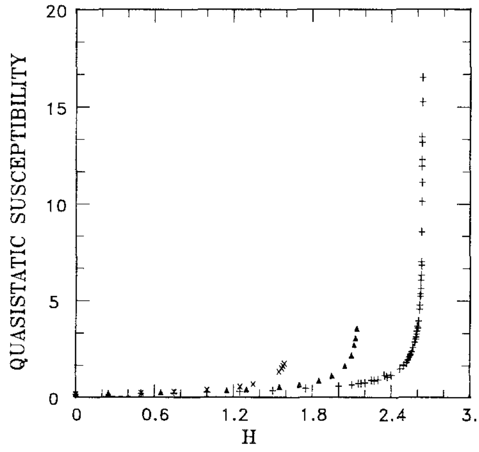

Fig. 4. Quasistatic susceptibility for $d=5$, 6, and 7 indicated by crosses, triangles, and pluses, respectively.

The behavior of χ_{qs} in seven dimensions is noticeably different. Here the quasistatic susceptibility increases more sharply than that of the other dimensions. For a system with length $L=9$ (i.e., 9^7+9^6 total spins) and a temperature $T=0.55T_c$, χ_{qs} increases by a factor of 110 from its value at the condensation point. This behavior is qualitatively the same as what is observed near the spinodal in a mean-field simulation.

In Fig. 5, the quasistatic susceptibility for the Curie–Weiss mean-field approximation is plotted along with data for the $d=7$ Ising model versus the reduced magnetic field Δh. Data for five different system sizes are shown. The temperature has been chosen for the Curie–Weiss model, so that the susceptibility at the condensation point matches that of the $d=7$ system. The numerical value for the presumed $d=7$ spinodal is chosen so that the data lie as close to the Curie–Weiss curve as possible.

As the system size increases, the $d=7$ data appear to approach the Curie–Weiss plot. The left-hand side of the curve is the asymptotic regime. Here the behavior approaches the expected scaling law near the spinodal[1]:

$$\chi_{qs} \sim (\Delta h)^{-1/2} \tag{5}$$

For each different system size there is a noticeable "tail" for small Δh where the plots end. A similar effect has been observed in data from Ising models with long-range interactions.[7] Since the tails depend upon system size, they are thought to be a finite-size effect. Otherwise, the $d=7$ data are

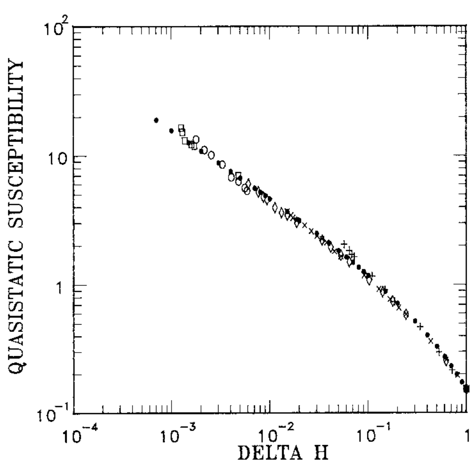

Fig. 5. Quasistatic susceptibility for $d=7$ Ising models fit to a mean-field prediction determined from a numerical evaluation of the Curie–Weiss partition sum. Bullets give the theoretical mean-field locus. Pluses, crosses, diamonds, circles, and squares indicate $d=7$ systems of size $L=3$, 4, 5, 7, and 9, respectively.

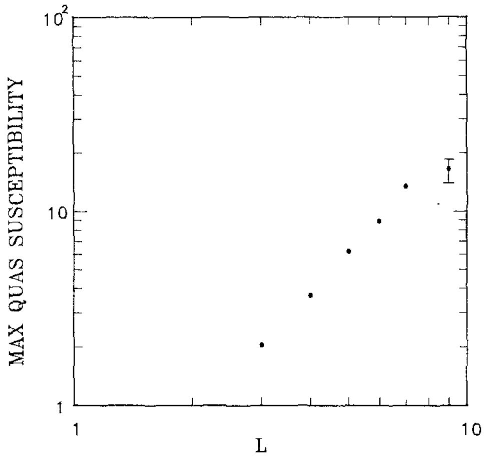

Fig. 6. Finite-size scaling plot for $d=7$ metastable Ising models. A least-squares fit gives a slope of 1.99.

approaching the Curie–Weiss behavior more closely as the system size is increased.

Finally, the behavior of χ_{qs} in the context of finite-size scaling is investigated. According to standard arguments, the system will feel its finite size when the correlation length ξ is equal to the length of the system L. For the spinodal, the correlation length scales with the reduced field as

$$\xi \sim (\Delta h)^{-1/4} \tag{6}$$

which, with Eq. (5), implies that the maximum quasistatic susceptibility $\chi_{\max}$ scales with L according to the relation

$$\chi_{\max} \sim L^2 \tag{7}$$

Figure 6 shows a log–log plot of $\chi_{\max}$ versus L. The error bars are largest for the $L=7$ and $L=9$ points. This is thought to be due to the effect of critical slowing down, which reduces the accuracy of the statistics. A least squares fit to the points gives a slope equal to 1.99, which agrees quite well with the predicted value 2 from Eq. (7). On the other hand, in six dimensions, $\chi_{\max}$ was found to be nearly independent of L.

5. CONCLUSION

The nucleation rate measurements appear to support the conjecture of the existence of spinodal singularities in nearest-neighbor $d=7$ Ising models as opposed to the domination of nucleation processes for $d = 5$ Ising models. The steeply dropping curves in Fig. 3 have effective slopes which are larger in magnitude than the maximum allowable slope calculated from classical nucleation theory. Unlike the $d = 5$ system, the $d = 7$ system does not monotonically cross over to the CNT regime from the unstable regime. The spinodal is a good candidate for an explanation of the $d = 7$ curves. As the system size is increased, the curves should approach a step function if a spinodal is present, so that there will be a sharp division between the unstable and metastable regimes in an infinite system. No nucleation events were observed between the presumed spinodal and coexistence curve.

The quasistatic susceptibility data are also consistent with the presence of a spinodal. The $d = 7$ curves appear to collapse reasonably well onto the Curie–Weiss mean-field spinodal curve in Fig. 5. Furthermore, a finite-size scaling analysis of the data agrees quite well with the behavior which would arise due to a spinodal singularity.

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REFERENCES

1. J. Gunton and D. Droz, *Introduction to the Theory of Metastable and Unstable States* (Springer, Berlin, 1983).
2. D. Stauffer, A. Coniglio, and D. W. Heermann, *Phys. Rev. Lett.* **49**:1299 (1982).
3. J. D. Gunton and M. C. Yalabik, *Phys. Rev. B* **18**:6199 (1978).
4. W. Klein and C. Unger, *Phys. Rev. B* **28**:455 (1983).
5. D. W. Heerman, W. Klein, and D. Stauffer, *Phys. Rev. Lett.* **49**:1262 (1982).
6. L. Monette, W. Klein, M. Zuckermann, A. Khadir, and R. Harris, *Phys. Rev. B* **38**:11607 (1988).
7. T. S. Ray and W. Klein, *J. Stat. Phys.*, to appear.
8. K. Huang, *Statistical Mechanics* (Wiley, 1963).
9. P. C. Hohenberg and B. Halperin, *Rev. Mod. Phys.* **49**:435 (1977).
10. K. Binder, ed., *Monte Carlo Methods in Statistical Physics* (Springer-Verlag, 1979).
11. W. Oed, *Appl. Informatics* **24**:358 (1982).

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