Spinodals in a Long-Range Interaction System

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A Monte Carlo study has been made of metastable states in the three-dimensional Glauber–kinetic-Ising model with long-range interactions. It is found that the properties of pseudospinodals converge rapidly with increasing interaction range to those predicted for the mean-field spinodal. A breakdown of the classical droplet model in the vicinity of this spinodal was also observed.

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Experimental data on metastable states, e.g., Monte Carlo simulations of the two-dimensional and three-dimensional Ising model with short-range interactions[1,2] and light scattering experiments,[3] gave no indication of a sharp spinodal line as predicted by mean-field theories. Such a spinodal line is a nearly unavoidable consequence of all assumptions that a (local) free energy density can be defined for metastable states, as a unique function of the local order parameter (and its gradient). If this spinodal line exists, then the susceptibility for magnetic systems or the compressibility for one-component systems should increase and go to infinity as this line is approached. In fact, one does observe an increase as one probes deep into the metastable region, but the system becomes unstable before one reaches the predicted spinodal line.[1] An extrapolation of these data then gives a pseudospinodal which does not constitute any evidence for an actual spinodal.

Here we present Monte Carlo simulations of the metastable state of a three-dimensional system with long-range interactions and pursue the question of the existence of a spinodal line.

In our simulations we used a model proposed by Domb and Dalton,[4] the equivalent-neighbor model. It bridges the gap between short-range interactions and the case of infinite-range interactions which gives a mean-field theory. Instead of the usual nearest-neighbor interactions of the Ising model, one assumes that each spin of the lattice interacts with neighbors over several lattice constants with a constant interaction energy J.

The Monte Carlo calculations of the metastable state of this model were done for interactions up to seven lattice constants, i.e., $q = 3374$ where q is the number of neighbors with which a given spin is interacting in a simple-cubic lattice with periodic boundary conditions. The interaction strength was $K = Jk_BT = \frac{9}{4}(1/q)$. These calculations were done for a system of size 32^3 with a new algorithm[5] which is especially suited for low temperatures (here $T/T_c \cong 0.45$). The basic new idea of the algorithm is to store for each spin i the sum $\sum_{(i,j)} \sigma_i \sigma_j$ ($\sigma = \pm 1$; j runs over the q neighboring lattice sites) which is needed to evaluate the Hamiltonian of the system. If during the Monte Carlo process the spin at the site i is flipped then this sum is updated for the site i and for the q neighboring spins. This greatly simplifies the Monte Carlo procedure. Within

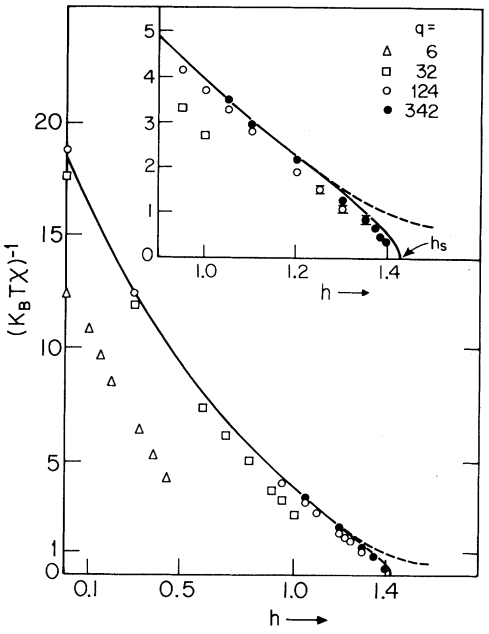

FIG. 1. Inverse susceptibility as a function of the dimensionless field for various interaction ranges. The full curve is the mean-field prediction at $T/T_c = \frac{4}{9}$. The spinodal is predicted at $h_s = 1.43$ where the field $h = 2\times$ (magnetic dipole) $\times$ (magnetic field)$/k_BT$. The broken curve is a fit of the classical droplet model. The only free parameter was fitted on our data near $h = 0$.

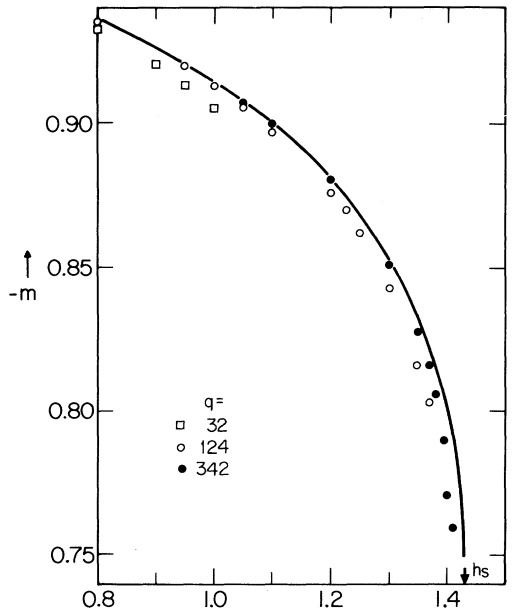

FIG. 2. Magnetization vs the dimensionless magnetic field. Magnetizations for $h = 1.4$ and 1.41 were determined by the flat part of the corresponding curves in Fig. 3(a). The solid curve represents the mean-field magnetization.

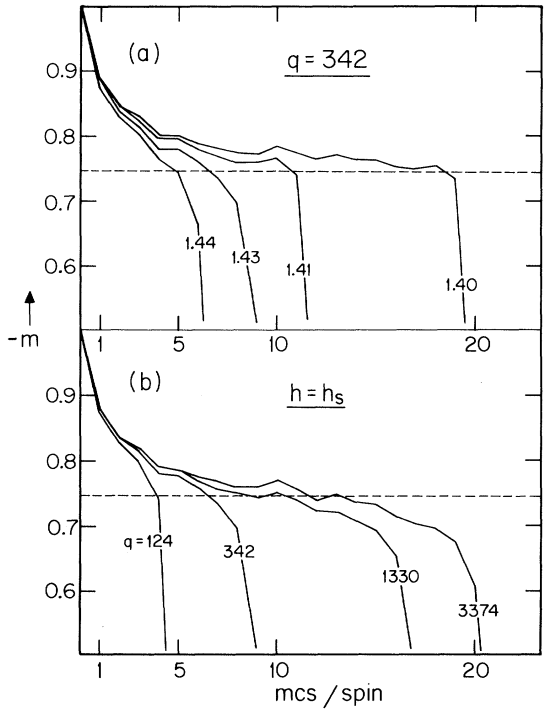

FIG. 3. Time evolution of the magnetization. The broken line represents the mean-field magnetization at the spinodal ($h_s = 1.43$). In (a) the field is varied for fixed interaction range, while (b) shows the evolution of the magnetization at fixed $h = h_s$ when the interaction range is varied. The magnetizations for $q = 1330$ and $q = 3374$ already exhibit a metastable state.

the limit of accuracy we could not detect finite-size effects by using 24^3 and 48^3 systems.

Figure 1 shows, for $q = 6, 32, 124, 342$, our data for the inverse susceptibility as determined by the magnetization fluctuations

$$\chi \propto \langle m^2 \rangle - \langle m \rangle^2 . \tag{1}$$

These susceptibilities are compared to mean-field theory for $T/T_c^{MF} = \frac{4}{9}$ (solid line), i.e., the limit $q \to \infty$, which predicts a spinodal point at a field $h_s = 1.43$. Clearly we cannot reach this point, but if we increase the number of neighbors q we can probe deeper into the metastable region and come closer to this point before the system becomes unstable, i.e., before the lifetime of the metastable state (defined by the "flat" part of the time-dependent magnetization[6]) becomes too short to extract reliable fluctuations. On the other hand, the lifetime of the metastable states quite close to the mean-field spinodal is sufficiently long to extract a magnetization (see Figs. 2 and 3) which can be used to determine the susceptibility. An extrapolation of these data yields a pseudospinodal point which approaches the predicted spinodal point with increasing interaction range. Our figures make clear that this convergence of pseudospinodals to the true infinite-range spinodal is quite rapid.

Let h_q^s denote the limiting h at which our system becomes unstable for a given q in the sense described above. We found that the ratio of the mean-field correlation length ξ^{MF} and the interaction range R of this limiting h_q^s was constant,

$$\xi^{MF}(h_q^s)/R \cong C , \tag{2}$$

where C is of the order of unity. This implies that one cannot measure pseudoequilibrium properties in the region where $\xi^{MF} \gg R$ and where deviations from mean-field behavior are expected.

Finally, let us look at the susceptibility given by the classical droplet model with a surface tension independent of field and radius (broken line),

$$\chi \propto \sum_s s^2 \exp(hs - \Gamma s^{2/3}) . \tag{3}$$

The coefficient Γ entering this susceptibility was fitted to the mean-field prediction for χ near the coexistence curve, where one expects the classical droplet model to work best (it should be noted that the surface tension Γ is the only free parameter in this fit). Surprisingly, the classical drop-

let model fits over a wide range. Only near the mean-field spinodal do we observe a breakdown of this model, as can be seen by the Monte Carlo data for $q=342$. Earlier comparison of the classical droplet model with Monte Carlo data[6] for $q=6$ did not show such a breakdown since one could not reach deep enough into the metastable region. However, such a breakdown was suggested by an analysis of renormalization-group flows.[7] Possible alternatives to the classical droplet model were also discussed in the same work. For the long-range interactions studied in this work, mean-field theory seems to describe our data better than the classical droplet model.

To summarize, our data show that pseudospinodals converge rapidly to the predicted mean-field spinodal with increasing interaction range and we have observed for the first time a breakdown of the classical droplet model. A more detailed description of this work will be contained in Ref. 8.

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[1]K. Binder, Ann. Phys. (N.Y.) 98, 390 (1976).

[2]D. Stauffer, A. Coniglio, and D. W. Heermann, to be published.

[3]B. Chu, F. J. Schoenes, and M. E. Fisher, Phys. Rev. 185, 185 (1969).

[4]C. Domb and H. W. Dalton, Proc. Phys. Soc., London 89, 859 (1966).

[5]D. W. Heermann, to be published.

[6]K. Binder, Phys. Rev. B 8, 3423 (1973).

[7]W. Klein, Phys. Rev. Lett. 47, 1569 (1981).

[8]D. W. Heermann, A. Coniglio, W. Klein, and D. Stauffer, to be published.

Photon-Stimulated Desorption of O^+ from Na_xWO_3: Demonstration of Bonding Site Selectivity

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Photon-stimulated desorption of O^+ ions has been obtained from Na_xWO_3 in the range $30\ \text{eV} < h\nu < 84\ \text{eV}$. The results show applicability of the Knotek-Feibelman interatomic Auger decay model for ion desorption and show the first observation of bonding-site selectivity in the process. The local coordination of the desorption site and the nature of the bonding which contributes to ion desorption are also discussed.

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Photon- and electron-stimulated desorption (PSD and ESD) of ions from surfaces are becoming important methods of studying surfaces and interfaces. The Knotek-Feibelman[1] (KF) mechanism was proposed to explain ESD of O^+ ions from the maximally valent oxides TiO_2, V_2O_5, and WO_3 at the *metal* core-level excitations through an interatomic Auger decay. For example, the W s and d electrons in WO_3 are stripped away and bound to the O ions. When a W core (e.g., W $5p$ level) is excited, the only way the core hole can decay is for an O (valence) electron to drop into the hole state. Emission of an Auger electron would then leave the O ion in a two-hole state. Since the equilibrium charge of the O ion in the crystal is of the order $O^{(1+y)-}$, $0<y<1$ (not O^{2-}), there is appreciable probability[1] that the O will desorb as O^+.

In ESD, atomic excitations are accomplished by electron bombardment, while in PSD, photons of energy $h\nu$ cause the excitation. In both spectroscopies, the number of desorbed ions is measured as a function of the energy of the incident beam. Since the KF decay mechanism is independent of the method of excitation of the core hole, the explanation of PSD results should follow the