RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 28, NUMBER 1 1 JULY 1983

Pseudospinodals, spinodals, and nucleation

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(Received 28 February 1983)

We develop a field-theoretic description of nucleation for systems with long-range interactions undergoing deep quenches. We find that the critical droplet can be related to a percolation cluster and has a fractal dimension less than the spatial dimension *d*. For $d > 6$ "spinodals" are found for any potential range *R*; in contrast, for $d < 6$ spinodals are found only for $R \rightarrow \infty$. We also compare our results to those of mean-field theory.

Classical (e.g., Becker-Döring) nucleation theory[1] has been shown to give a good description of the decay of the metastable state in $d=3$ nearest-neighbor Ising models far from the critical point[2] and is thought to be a good description of nucleation in fluids.[3] Cahn and Hilliard[4] and Langer[5] have formulated field theories that relate the critical droplet in classical nucleation to a spatially nonuniform saddle-point solution of a Ginzburg-Landau "ψ^4" model. Such a field-theoretic formulation has led to significant insight into the nucleation process.[3]

Recently it was proposed by one of us that noncompact fluctuations are important in deep quenches in metastable states.[6] In order to obtain quenches of sufficient depth it was necessary to study models with interactions of longer range than nearest neighbor.[7] Monte Carlo simulations on such models suggest that the dominant fluctuations in deep quenches are noncompact[8] and that critical (i.e., nucleating) droplets may also be ramified.[9]

In this work we present a field-theoretic description of nucleation in systems undergoing deep quenches based on the standard Ginzburg-Landau ψ^4 free-energy functional[5]

$$\tilde{F}(\psi) = \int d\vec{x} \{ (a/2) R^2 [\nabla \psi(x)]^2 - b\psi^2(x) + c\psi^4(x) - h\psi(x) \} \; , \tag{1}$$

where h is proportional to the applied magnetic field, R is the interaction range, a and c are constants, and b is proportional to $T/T_c - 1$ and is negative for $T < T_c$. The partition function $\tilde{Z}(h)$ is defined by the functional integral

$$\tilde{Z}(h) = \int \delta\psi \, e^{-\tilde{F}(\psi)} \; . \tag{2}$$

The mean-field approximation for the free energy $\bar{F}(\bar{\psi})$ is obtained by setting the gradient equal to zero in Eq. (1) and replacing ψ by its most probable value $\bar{\psi}$. For $T < T_c$ the free energy has the form of the standard double-well potential [see Fig. 1(a)].[3] For $h=0$ the wells are of equal depth and as $|h|$ increases one well becomes shallower than the other [see Fig. 1(b)]. That value of $h = h_s$ for which the shallow well disappears [see Fig. 1(c)] locates the classical spinodal.[10] It is straightforward to obtain the value of $\bar{\psi}$ at the spinodal

$$\bar{\psi}_{\text{sp}} = -[(|b|/6c)]^{1/2} \; . \tag{3}$$

It is important to note that the mean-field free energy is the result of an exact calculation of $\tilde{Z}(h)$ in the limit[4] $R \rightarrow \infty$.

In order to investigate quenches near the region of the mean-field spinodal, we define a new field,

$$\phi(x) = [\psi(x) - \bar{\psi}_{\text{sp}}] R\sqrt{a} \; . \tag{4}$$

Equation (1) can be written as

$$\tilde{F}'(\phi) = \int d\vec{x} \{ \tfrac{1}{2} [\nabla \phi(x)]^2 + \epsilon\phi(x) - \alpha\phi^3(x) + (c/R^4A^2)\phi^4(x) \} \; , \tag{5}$$

where $\epsilon = (h_s - h)/(R\sqrt{a})$ and $\alpha = (6|b|c)^{1/2}/(AR)^3$. We

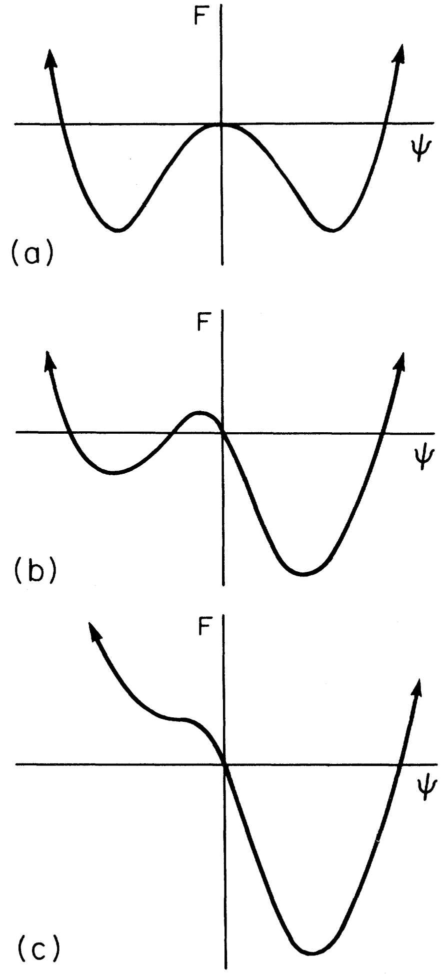

FIG. 1. ψ^4 mean-field free energy for $T < T_c$ as a function of the order parameter ψ. (a) is for $h=0$, (b) for $0 < h < h_s$, and (c) for $h = h_{\text{sp}}$.

now restrict our considerations to that region of thermodynamic space near the classical spinodal, hence $\phi(x) << 1$. This requires that $R >> 1$ and $\epsilon << 1$. In this region we can, to a good approximation, neglect the $\phi^4(x)$ term. We have, therefore,

$$\tilde{F}'(\phi) \simeq F(\phi) = \int d\vec{x} \{ \tfrac{1}{2} [\nabla \phi(x)]^2 + \epsilon\phi(x) - \alpha\phi^3(x) \} \ . \tag{6}$$

The mean-field approximation for the free-energy functional of Eq. (6) has one minimum and one maximum (see Fig. 2).

Following Cahn and Hilliard[4] and Langer[5] we now search for nonuniform solutions of the Euler-Lagrange equation,

$$- \nabla^2 \phi(x) + \epsilon - 3\alpha\phi^2(x) = 0 \ . \tag{7}$$

These solutions are saddle points of the free-energy functional of Eq. (6) and describe the profile of the critical droplet.

We assume the droplet is spherically symmetric and that the interface can be considered flat, so that Eq. (6) becomes

$$- d^2\phi(x)/dx^2 + \epsilon - 3\alpha\phi^2(x) = 0 \ . \tag{8}$$

We return to the flat interface approximation below. The solution of Eq. (8) is

$$\phi(x) = \sqrt{\epsilon/3\alpha} \{ -1 + 3/\cosh^2[(\tfrac{3}{4}\epsilon\alpha)^{1/4} x] \} \ .$$

In order to obtain the exponential part of the lifetime of the metastable state, which describes the nucleation barrier, we make the following variable transformations in Eq. (6),

$$\phi(x) = (\epsilon^{1/2}/\alpha^{1/2}) u(s), \quad s = \epsilon^{1/4}\alpha^{1/4} x \ . \tag{10}$$

Equation (6) becomes

$$\bar{F}(u) = \{ \epsilon^{3/2} / [(\epsilon\alpha)^{d/4} \alpha^{1/2}] \} \times \int d\vec{s} \{ [\nabla_s u(s)]^2 + u(s) - u^3(s) \} \ . \tag{11}$$

The coefficient in front of the above integral is proportional to R^d. For large R, therefore, the partition function can be approximated by a steepest-descent integral that is evaluated in the neighborhood of two saddle points. One saddle point is associated with the spatially uniform metastable state (i.e., $\bar{\psi}$) and the other with the critical droplet [Eq. (9)]. Due to the negative cubic term in Eq. (11), the steepest-descent integral will not converge as $u \rightarrow +\infty$, and the contour will have to be deformed into the complex plane.[5,11] This deformation will give rise to an imaginary part of the free energy which can be related to the lifetime of the metastable state. The lifetime τ will be of the form

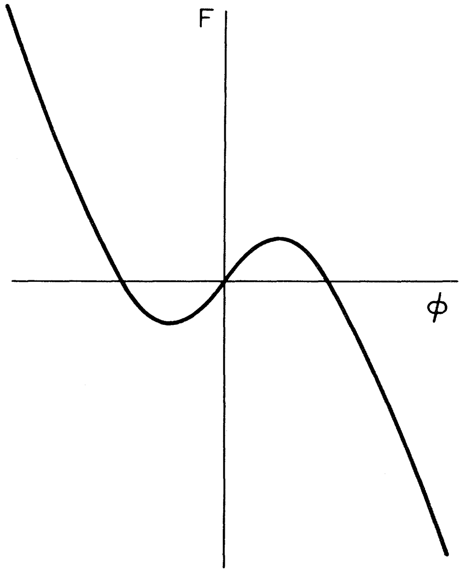

FIG. 2. "ϕ"^{3} mean-field free energy as a function of ϕ for $h < h_s$ and $T < T_c$.

$$\tau = f(\epsilon, \alpha) \exp\{ c\epsilon^{3/2} / [(\epsilon\alpha)^{d/4} \alpha^{1/2}] \} \ , \tag{12}$$

where c is a constant and $f(\epsilon, \alpha)$ is a function that is slowly varying compared to the exponential for large R.

Equations (9), (11), and (12) are the central results of this work. Before discussing the physical implications of these equations, we briefly discuss the flat interface approximation. This approximation is certainly not exact; however, all conclusions discussed below will rely only on the existence of a nonuniform bounded solution of

$$-\frac{d^2u(s)}{d^2} - \frac{d-1}{s} \left(\frac{du(s)}{ds} \right] + 1 - 3u^2(s) = 0 \ , \tag{13}$$

obtained from the functional derivative of Eq. (11) and the assumption of spherical symmetry. The solution must also have the property that as $s \rightarrow \infty$ $u(\infty) = -\sqrt{1/3}$. It can be shown that such a solution exists.[11] The differences between the use of the planar interface solution given in Eq. (9) and the true solution of Eq. (13) will be in the value of c and the form of $f(\epsilon, \alpha)$ in Eq. (12).

There are several conclusions to be drawn from Eqs. (9), (11), and (12). The first point to make is that the coefficient $\epsilon^{3/2}[(\epsilon\alpha)^{d/4} \alpha^{1/2}]$ is proportional to

$$R^d (h - h_s)^{(3/2) - (d/4)} = K \ . \tag{14}$$

The saddle-point evaluation of the integral

$$Z(h) = \int \delta u e^{-\bar{F}(u)} \tag{15}$$

will be exact in the limit $K \rightarrow \infty$; it should, however, be a good approximation for large K. From Eq. (14), the large-K limit implies for $d < 6$ that $R >> 1$ and h is not too near the mean-field spinodal value. However, for $d > 6$ the saddle-point integral becomes a very good approximation for $h - h_s << 1$, for all R.

The equation for the lifetime of the metastable state [Eq. (12)] also exhibits interesting differences above and below $d = 6$. From the above discussion it is clear that for $d > 6$ and for $R \simeq 1$ the exponential part of the lifetime of the metastable state increases as h approaches h_s. However, for $d < 6$ and R, $K >> 1$ the exponential part of the lifetime of the metastable state decreases as h approaches h_s, similar to the result of Cahn and Hilliard.[4,12] These results seem to indicate, consistent with other work,[6,13] that $d = 6$ is a critical dimension above which certain aspects of the mean-field theory of spinodals are correct.

The difference between the behavior of the lifetimes above and below $d = 6$ can be understood by calculating the free-energy cost of creating a critical droplet. If we define $\phi(\infty)$ as the value of $\phi(x)$ at $x = \infty$ in Eq. (9), then the free-energy cost is given by

$$\int d^dx \{ \epsilon[\phi(x) - \phi(\infty)] - \alpha[\phi^3(x) - \phi^3(\infty)] \} \ . \tag{16}$$

The free-energy cost is proportional to $\epsilon^{(3/2)-(d/4)}/\alpha^{(1/2)+(d/4)}$. We can see that as $h \rightarrow h_s$, $\epsilon \rightarrow 0$ and for $d<6$ the excess free energy goes to zero while for $d>6$ it diverges.

It is important to understand what information the above equations contain about spinodals. Above $d=6$ it would appear that Eq. (12) indicates the existence of a well-defined classical spinodal at $h=h_s$ for finite R. This conclusion is based on the existence of an infinite lifetime τ at $h=h_s$ so that statements about thermodynamics make sense. The same thing can be said for $d<6$ and $R \rightarrow \infty$. There is, however, one crucial difference in these two cases.

The quantity h_s depends on the constants a, b, and c in Eqs. (1). These in turn depend on how the field or coarse-grained variable $\psi(x)$ is defined. For $R \rightarrow \infty$ the procedure gives unique values for a, b, and c; however, for finite R there appears to be no unique procedure for any finite dimension.[14] Different coarse graining procedures give different values of a, b, and c, and hence different values of h_s. These different values imply that above $d=6$ there exist well-defined spinodal exponents, but the location of the spinodal is not well defined. The physical implications of this impreciseness are discussed in detail elsewhere.[6]

For $d<6$ and R finite, the argument of the exponential in τ goes to zero and h approaches h_s. This implies that even if there were a spinodal at $h=h_s$ it could not be described by this theory. However the "spinodal" can be approached as closely as one wishes by making R larger. This will result in apparent singularities in thermodynamic quantities—the so-called pseudospinodal.[7]

Finally we argue that the critical droplet is ramified (as defined below) and has in fact a structure that can be thought of in terms of a percolation model. It has been shown that the Ising critical point can be described in terms of a percolation model.[15,16] The model is the correlated-site random-bond model where one has a d-dimensional Ising model and considers sites with spin down to be occupied. Bonds are then distributed with a random probability between any two occupied sites. These bonds can connect occupied spins at arbitrary distances. This model can be shown to be the $s \rightarrow 1$ limit of the dilute s-state Potts model[16] with the Hamiltonian

$$-\beta H = J \sum_{ij} (s\delta_{\sigma_i \sigma_j} - 1) n_i n_j - \sum_{ij} n_i n_j - \Delta \sum_i n_i + H \sum_i (s\delta_{\sigma_i 1} - 1) n_i \ , \qquad (17)$$

where n_i can have the values 0 or 1, $\delta\sigma_i\sigma_j$ is the Kronecker delta, Δ is the chemical potential which is a function of K and h, h is the Ising field, and H is the Potts field.

The free energy of this model in the mean-field approximation is given by[15]

$$F = \tfrac{1}{2}(s-1) r_1 \tilde{\phi}^2 - (1/3!) w_1 (s-1)(s-2) w_1 \tilde{\phi}^3 - \tfrac{1}{2} w_2 (s-1) \psi \tilde{\phi}^2 + \tfrac{1}{2} b \psi^2 + c\psi^4 - h\psi - (s-1) H \tilde{\phi} \ , \qquad (18)$$

where b, c, and h are as defined above. The factors w_1 and w_2 are finite and nonzero, and r_1 is a function of J. The quantities $\tilde{\phi}$ and ψ are the percolation and Ising-order parameters, respectively. The Ising problem can be recovered by setting $s=1$. The percolation free energy is given by[17] $dF/ds|_{s=1}$.

At the spinodal,

$$\left.\frac{dF}{ds}\right|_{s=1} = (\tfrac{1}{2})(r_1 - w_2\psi_{\text{sp}})\tilde{\phi}^2 + (1/3!) w_1 \tilde{\phi}^3 - H\tilde{\phi} \ . \qquad (19)$$

If J is chosen so that

$$r_1 - w_2 \psi_{\text{sp}} = 0 \ , \qquad (20)$$

then the mean-field spinodal line coincides with a percolation line.[18] From Eq. (19) one easily sees that the percolation exponents are the same as the spinodal exponents. In particular, the correlation length ξ and the connectedness length ξ_p diverge with the same exponent as do the susceptibility and the mean cluster size. Consequently, a droplet description at the spinodal can be obtained using percolation clusters as droplets in a way similar to what is done at the critical point.[15,16] As a consequence, a fractal dimension[19] $d_f < d$ can be assigned to the fluctuations at the spinodal. We define these fluctuations to be ramified.

In the standard nucleation picture, and in its field-theoretic representation, fluctuations up to the critical droplet size are considered quasiequilibrium fluctuations about the relative minimum of the free energy. Consequently standard equilibrium concepts should be applicable to such fluctuations. In particular, from Eq. (9) we see that the radius of the critical droplet r_c is proportional to

$$(\epsilon\alpha)^{-1/4} \simeq R(h-h_s)^{-1/4} \ ; \qquad (21)$$

however, $R(h-h_s)^{-1/4}$ is proportional to the correlation length ξ at the spinodal, even in the limit[20] $R \rightarrow \infty$. The critical droplet then can be considered as a percolation cluster with $d_f < d$.

To summarize, we have presented a field-theoretic description of nucleation of Ising-type systems undergoing deep quenches. We have found that the nucleating droplet is ramified (i.e., has $d_f < d$) in agreement with computer simulations in $d=3$ Ising models.[8] We also found that for $d>6$ the exponential part of the lifetime of the metastable state increases as the spinodal is approached in agreement with meanfield treatments[4,11] but decreases as the spinodal is approached for $d<6$.

ACKNOWLEDGMENTS

We are pleased to acknowledge useful and stimulating discussions with K. Binder, E. T. Gawlinski, J. D. Gunton, D. W. Heermann, A. Sawyer, and D. Stauffer. One of us (C.U.) gratefully acknowledges the support of a National Science Foundation (NSF) fellowship. The Center for Polymer Studies is partially supported by grants from NSF and the Army Research Office.

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