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Initial-growth modes of nucleation droplets

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Using the theoretical formulation of Cahn and Hilliard and of Langer, we study the initial growth of nucleation droplets in systems with no conservation law for various dimensions and for an arbitrary distance from the coexistence curve. In the vicinity of the coexistence curve the nucleating droplets are compact at the center and growth occurs only at the droplet surface. Close to the classical spinodal the nucleating droplets are ramified and the growth occurs preferentially at the droplets' center. The growth is always maximum where the second derivative of the free-energy density is negative, i.e., at unstable concentrations. The droplet profile for any specified field tends to a universal $\tanh(x)$ profile for large dimension. We argue that certain aspects of the droplet depend only on a single scaling field that combines dimension and quench depth.

Metastable states can occur at almost any first-order phase transition; the metastable states exist for a finite time before the system decays to the absolutely stable state.[1] Recently there has been increasing evidence that metastable states can decay by several different modes.[2–5] Classical nucleation theory[1,6] assumes a metastable state decays, or nucleates, through the formation of a compact and localized fluctuation of the stable phase. By compact we mean that the volume of the drop V is related to its linear size l through $V \propto l^d$, where d is the spatial dimension. These droplets grow by increasing their radius by accreting matter at their surface.[7,8]

Classical nucleation theory predicts a smooth crossover between metastability and instability, while mean-field theory predicts a sharp spinodal dividing line. Heerman and Klein[3,9] studied nucleation in the three-dimensional Ising model for various interaction ranges with the use of Monte Carlo simulation. Nucleation from metastable states far from the coexistence curve showed significant deviations from the classical theory.[3,9] The droplets become of small amplitude and ramified having a fractal dimension[10] d_f smaller than the dimension of space.[3] That is, $V \propto l^{d_f}$ with $d_f < d$.

We have previously obtained[4,5] a description of these ramified droplets occurring near the classical spinodal starting with the field theoretic Landau-Ginzburg-Wilson[4] free-energy functional[7]

$$F(\psi) = \int d\mathbf{r}[R^2/2(\nabla\psi)^2 + f(\psi)] \ , \tag{1}$$

where $f(\psi) = \alpha\psi^4 - \epsilon\psi^2 + h\psi$ is the free-energy density for a uniform state; h is proportional to the external magnetic field; ϵ is proportional to $(T_c - T)/T_c$; α is a positive constant and R proportional to the range of the interaction. The metastable state remains well defined for fields right up to the spinodal field $h_s = (8\epsilon^3/27\alpha)^{1/2}$ for $R \to \infty$.[5,11]

In this Rapid Communication we treat with these techniques the initial stages of the nucleation and growth of droplets as the field and dimension change. The crossover between spinodally assisted nucleation near the classical spinodal and classical nucleation near the coexistence curve is shown to occur smoothly over a range of magnetic fields. The growth mode remains peaked where the second derivative of the free-energy density is negative, leading to an analogy with classical spinodal decomposition theory. Finally, this same crossover is shown to occur as a function of dimension, and a scaling field is conjectured.

For long-range interactions the nucleating droplet profile is expected to be a stationary point of the free-energy functional and satisfy[7,12] the Euler-Lagrange equation:

$$\left.\frac{\delta F}{\zeta\psi}\right|_{\bar\psi} = -R^2\left(\frac{d^2}{dr^2} + \frac{(d-1)}{r}\frac{d}{dr}\right)\bar\psi + 4\alpha\bar\psi^3 - 2\epsilon\bar\psi + h = 0 \ . \tag{2}$$

The solutions to Eq. (2) that correspond to the metastable and stable states are independent of r ($\psi = \psi_{MS}$ and $\psi = \psi_S$, respectively) and are local minima of $F(\psi)$. The nonconstant solution to Eq. (2) with boundary condition $\bar\psi(\infty) = \psi_{MS}$ is a saddle point of $F(\psi)$ and corresponds to a localized fluctuation away from the metastable phase; this fluctuation is the nucleating droplet.

The direction in which the free energy $F(\psi)$ decreases as the solution moves away from the saddle point corresponds to the initial growth mode of the droplet (within a quasistatic approximation).[7] If we rewrite the droplet profile as the nucleating droplet plus a small deviation, $\psi(r) = \bar\psi(r) + v(r)$, we can expand $F(\psi)$ to second order in v: $F(\psi) = F(\bar\psi) + F''(v)$, where

$$F''(v) = \int d\mathbf{r}\left[R^2/2(\nabla v)^2 + \left.\frac{\partial^2 f}{\partial\psi^2}\right|_{\bar\psi} v^2\right] \ . \tag{3}$$

Thus, the solutions to the Schrödinger equation

$$\left[-R^2/2\left(\frac{d^2}{dr^2} + \frac{(d-1)}{r}\frac{d}{dr}\right) + 12\alpha\bar\psi^2 - 2\epsilon\right]v_n(r) = w_n v_n(r) \tag{4}$$

are the normal modes of the system near the nucleating droplet configuration.[7] There is exactly one mode with a negative eigenvalue[7,13,14] corresponding to an instability; this growth mode will initially increase exponentially.

This stability analysis is independent of the detailed dynamics of the system, and thus rates of growth and the behavior in later stages of growth must depend on other factors affecting the dynamics. For the Ising model with Glauber dynamics, the initial growth mode predicted by the full dynamical theory is identical to the growth mode obtained by linear stability analysis. Depending on the relative sizes of the nucleation time, the droplet growth time, and the time needed to move material across the radius of the droplet, the initial growth mode derived below (valid for infinitesimal times) may be independent of the dynamics and be valid for several dynamical universality classes.

As the dimension is raised for fields near the spinodal value, the droplet crosses over from a ramified droplet for low dimensions to a compact droplet (having a concentration at its center approximately the concentration of the stable phase) for large dimensions. This can be seen by regarding Eq. (2) as an equation of motion for a damped particle in a potential: r is the time; $\bar{\psi}$ is the displacement; $-f$ [in Eq. (1)] is the potential; and the cubic polynomial in Eq. (2) is the force.[7] Near the spinodal for low dimensions, where the metastable peak in $-f$ is at much higher free energy than the stable peak, the particle never passes close to the stable peak. As $(d-1)$ increases, the damping increases, and the particle must start with more energy (i.e., higher on $-f$ and closer to the stable peak) to have the potential energy of the metastable peak at $r=\infty$.

We examine the behavior of the solutions to Eq. (2) by studying an approximate equation appropriate for large dimension. For low dimensions, the damping term $[(d-1)/r]d/dr$ is less important and ignoring it does not change the scaling of the solution.[5] For very large dimensions this damping term becomes more important, and only for very large r [where $(d-1)/r$ is small] should the solution be determined again by inertial effects. So, for large dimensions and h near h_s we ignore the second derivative and study the solution to

$$-R^2\frac{(d-1)}{r}\frac{d\psi}{dr}+4\alpha\psi^2-2\epsilon\psi+h=0 \ , \tag{5}$$

which is

$$-k\exp\{-r^2/[2(d-1)R^2]\}=\{[\psi(r)-a\sqrt{\Delta h}\,]/[\psi(r)+a\sqrt{\Delta h}\,]\}^{1/b\sqrt{\Delta h}}\{1/[\psi(r)-\psi_s]\} \ , \tag{6}$$

where a and b are constants, $\Delta h=h_s-h$, and k is an integration constant which must be fixed by the boundary condition. Since the linear and second derivative terms scale identically with and r,[5] this solution should scale correctly with R, ϵ, α, and Δh.

In order to understand the physics described by Eq. (6) we investigated two asymptotic cases. In the first case we assume that the system is quenched to hear the spinodal and $\psi(r)\sim\sqrt{\Delta h}$ for all r.[5] To determine k we must use the boundary condition that $\psi(r=\infty)=\psi_{\rm MS}$. Unfortunately the solution in Eq. (6) is not a valid description for $r\geq(d-1)R$. In order to obtain k we will make the approximation that for $r\geq(d-1)R$ the solution of Eq. (2) neglecting the *first-order derivative* is valid,[4] while this assumption and the following matching condition are only approximate, the resulting scaling forms should be insensitive to the detailed approximations, since both derivative terms scale similarly:[5]

$$\tilde{\psi}(\tilde{x})=\sqrt{\Delta h}\,[-1+3/\cosh^2(\sqrt[4]{\Delta h}\,\tilde{x}/R)] \ .$$

To obtain k then we demand that at $x=(d-1)R$, $\tilde{\psi}(\tilde{x})=\psi(x)$ and $d\tilde{\psi}(\tilde{x})/d\tilde{x}=d\psi(x)/dx$.

With this method it can be seen[15] that

$$(k\psi_s)^{b\sqrt{\Delta h}}=c\exp[b(d-1)\sqrt{\Delta h}/2] \ , \tag{7}$$

where c is a constant. Using Eq. (7), Eq. (6) becomes, for Δh small,

$$\psi(r)=\{1+c\exp[b(d-1)\sqrt{\Delta h}/2]\exp[-r^2\sqrt{\Delta h}/2(d-1)R^2]\}/(1-c\exp[b(d-1)\sqrt{\Delta h}/2]\exp[-r^2\sqrt{\Delta h}/2(d-1)R^2]\} \ . \tag{8}$$

An interesting situation occurs with $r=0$, Eq. (8) becomes

$$\psi(0)=\frac{1+c\exp[b(d-1)\sqrt{\Delta h}/2]}{1-c\exp[b(d-1)\sqrt{\Delta h}/2]} \ . \tag{9}$$

If Δh or d is increased $\psi(0)$ becomes negative while $\psi(r=(d-1)R)$ is positive. This is clearly unphysical. Near the center of the droplet for $(d-1)R\sqrt{\Delta h}$ large enough the scaling solution is not valid. This implies that the ψ^4 term cannot be neglected and that the center of the droplet is more compact than the edges. This point should be stressed. The equation predicts that for fixed d as Δh becomes larger the center of the droplet becomes more compact; this effect is readily seen in the numerical solution to the full equation presented below. This then describes how the droplet which is ramified for Δh small starts to evolve into the compact droplet seen for $h\sim 0$; that is, it begins to compactify in the center. This is reminiscent of the growth of ramified critical droplets after nucleation.[3,5]

In order to describe the movement of the compact part of these hybrid droplets (i.e., compact core and ramified "halo"), we consider the center of droplets in systems shallowly quenched where $\psi(x)\sim\psi_s$. In this region Eq. (6) becomes

$$\psi(r)-\psi_s=-k^{-1}\exp[r^2\sqrt{\Delta h}/2(d-1)R] \ . \tag{10}$$

From $f(\psi)$ in Eq. (1) it is simple to see that ψ_s is of the form for small Δh, $\psi_s=\psi(0)-w\Delta h$, where w is a positive constant. With Eq. (9), we obtain $k=\tilde{c}e^{d-1}/[\psi(0)-w\Delta h]$, so that

$$\psi(r)+w\Delta h\simeq\psi(0)+\exp[r^2\sqrt{\Delta h}/2(d-1)R][\psi(0)-w\Delta h]/e^{d-1} \ . \tag{11}$$

We have also solved Eqs. (2) and (4) numerically for the nucleating droplet and growth mode profiles for several fields and dimensions; the details will be reported elsewhere.[15] Figure 1 shows the resulting nucleating droplet and initial growth mode profiles for several fields in three dimensions. The nucleating droplet near the spinodal is a small amplitude fluctuation that has been shown to have the ramified structure of a percolation cluster.[5] The growth mode is peaked at the droplet's center, corresponding to growth through compactification. In contrast, the droplet for $h \lesssim 0.4h_s$ is a large fluctuation (radius $\alpha 1/h$) of the stable phase at its center, with a bulk stable-metastable phase interface separating the interior and exterior of the droplet. The growth mode is peaked at the surface of the droplet; the droplet grows by simply increasing its radius with a constant interface shape.[6,7] The profile shape seems to depend only on the scaling field $z=(h_s-h)^{1/d-1}$ to within a few percent, for z not too small.[14]

The growth mechanism for intermediate fields is a mixture of radial growth and compactification. For all fields, however, the peak of the growth mode occurs at a radius (or concentration) where the second derivative of the free-energy density is negative: that is, $\partial^2 f/\partial\psi^2|\psi(r_{\max})<0$, where $r_{\max}$ is the location of the maximum initial growth. This can be seen by examining each term in Eq. (4). The eigenvalue ω must be negative for the mode to grow in time rather than decay. The term $-d^2v/dr^2$ must have the same sign as v since the growth mode curves toward the axis at its maximum. Furthermore, if the maximum of the growth mode occurs at $r\neq 0$, the linear derivative term is zero at that point; if the maximum occurs at $r=0$, a Taylor series expansion of v shows that the first derivative term is $(d-1)$ times the second derivative, and thus has the same sign. Hence, $\partial^2 f/\partial\psi^2$ must be negative at the growth mode maximum if ω is to be negative.

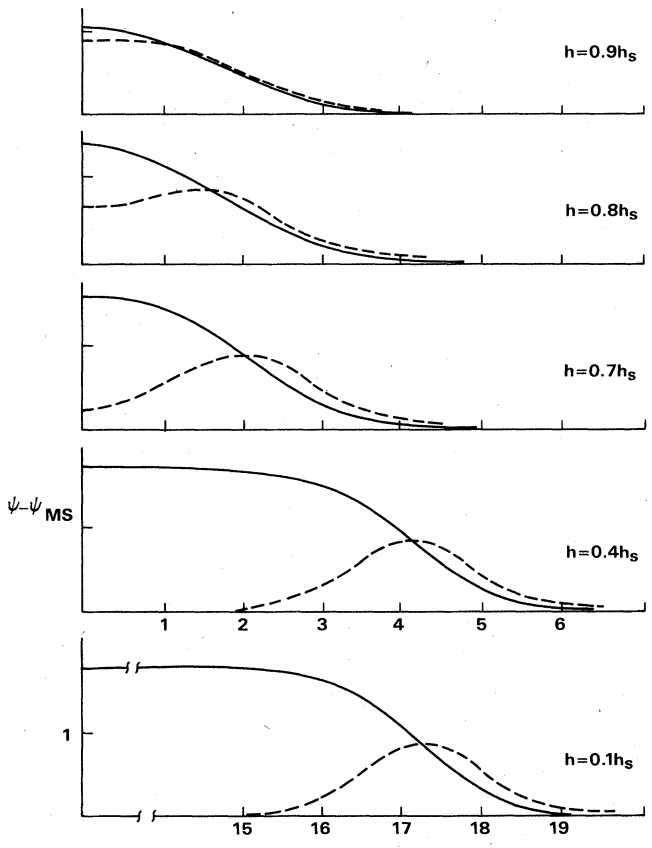

FIG. 1. Plot of nucleation-droplet and growth-mode profiles in three dimensions. The solid line is the nucleation-droplet profile; the dotted line is the growth-mode profile.

The condition of negative second derivative is the same condition as for growth of fluctuations in spinodal decomposition. While it is well accepted that there is a smooth crossover between nucleation and growth and spinodal decomposition, no one has developed a dynamical theory showing the same process occurring on both sides of a "spinodal." The linear stability analysis presented in this paper shows that both spinodal decomposition and growth of all droplets, both ramified and compact, can be regarded as an unstable phase separation of the droplet's surface or the system's bulk.[15] A more complete dynamical theory based on this approach, along the lines of the extensions of the simple Langer-Cahn-Hilliard theory,[11,16] may be able to prove the smooth crossover.

While the ramified nucleation droplets and changing growth modes have been seen in computer experiments,[3] it is important to search for them in physical systems as well. For most experimental systems, however, if the nucleation time is short enough so that there are sufficient droplets to measure, then the growth (or compactification) time is also so short that the effects of ramified droplets would be unobservable. In systems with long-range potentials one may, by properly adjusting the range of the interaction and the distance from the spinodal, be able to produce a sufficient number of long-lived droplets to measure their ramified structure by neutron scattering. This point is currently being investigated.[15] It is perhaps useful to briefly discuss the reason why initial growth can be described with the quasiequilibrium picture of Langer. As can be seen in both Langer's work[7] and ours[5] (and also from the dynamical models), the eigenvalue that describes initial growth goes to zero as the radius of the critical droplet diverges. It can be shown[15] that the vanishing of the eigenvalue implies that the droplet grows quasistatically compared with relaxation times both in the droplet bulk and in the metastable phase. This quasistatic growth makes possible the treatment with Langer's methods. A more detailed analysis will appear elsewhere.[15]

We have described the crossover between classical nucleation theory and spinodally assisted nucleation. This crossover occurs as *either* the quench depth is decreased, *or* as the dimension is raised. The maximum of the initial growth must always occur where the second derivative of the free-energy density is negative. This suggests that the dynamics of compact or ramified droplets as well as unstable fluctuations are at some level equivalent, all having to do with the compactification of ramified regions of the stable phase.

We have found an approximate scaling relating the change of the nucleating droplet with field and dimension. The ramified nucleating droplets also become more compact as they grow and time increases. We are currently extending this work by examining whether there is an extended scaling relating the compactification of the droplets with time, field, and dimension.

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