Fractals and Multifractals in Early-Stage Spinodal Decomposition and Continuous Ordering

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(Received 20 April 1990)

Systems undergoing spinodal decomposition often exhibit an interconnected morphology similar to a fractal in the early stage. It has been speculated that this early-stage structure is in fact a fractal. In this Letter I show that the linear theory of spinodal decomposition does indeed predict that the early-stage morphology is fractal and, in addition, has what one might call a multifractal structure. In contrast, there is no fractal or multifractal structure in continuous ordering. In addition, I construct percolation cluster growth models isomorphic to spinodal decomposition and continuous ordering so that precise tests of these predictions can be performed.

PACS numbers: 64.60.Fr, 05.50.+q, 05.70.Fh, 64.60.My

Systems undergoing spinodal decomposition[1] often exhibit an interconnected structure strongly reminiscent of fractals. It has been speculated that the early-stage morphology of spinodal decomposition is in fact fractal. Desai and Denton[2] have measured the fractal dimension d_f of a Lennard-Jones fluid undergoing spinodal decomposition in dimension $d=2$ and found $d_f \sim 1.4$. In addition, Coniglio and Zannetti[3,4] have shown that spinodal decomposition in the mean spherical model has an anomalous scaling behavior which they argue is multiscaling. They speculate that this multiscaling is associated with an underlying multifractal structure.

In this Letter I present an analysis of the order-parameter evolution, rather than the structure factor, indicating that the early-stage morphology is fractal and, in addition, has a multifractal structure. By early stage I mean that part of the evolution which is governed by the linear theory of Cahn and Hilliard.[5,6] I also present a mapping of the spinodal decomposition and continuous ordering evolution onto a percolation, or more accurately, a growing cluster problem.

I begin with the equations[1] for the evolution of the order parameter in models A (a nonconserved order parameter, which exhibits continuous ordering) and B (a conserved order parameter, which exhibits spinodal decomposition) in the Hohenberg-Halperin classification;[7]

$$\frac{\partial\psi(\mathbf{x},t)}{\partial t} = -M\Gamma\{-R^2\nabla^2\psi(\mathbf{x},t) - |r_0|\psi(\mathbf{x},t) + 4u\psi^3(\mathbf{x},t) - h\}. \quad (1)$$

In model A, Γ is a constant, which we will set equal to 1, and equals ∇^2 in model B. The constant M is a mobility, R is the range of the potential of interaction, T_c is the critical temperature, r_0 is proportional to $(T-T_c)/T_c$ and is assumed to be negative, u is a constant, and the applied magnetic field h can be set equal to zero in model B.

Assuming the order parameter has the form $\psi(\mathbf{x},t) = \psi_0 + u(\mathbf{x},t)$, where ψ_0 is a constant for which the right-hand side of Eq. (1) vanishes and $u(\mathbf{x},t)$ is small for early time, Eq. (1) is linearized to obtain

$$\lambda\phi(\mathbf{x}) = -M\Gamma\{-R^2\nabla^2\phi(\mathbf{x}) - |r_0|\phi(\mathbf{x}) + 12u\psi_0^2\phi(\mathbf{x})\}, \quad (2)$$

where $u(\mathbf{x},t)$ is assumed to be a linear combination of eigenvectors of the form $e^{\lambda t}\phi(\mathbf{x})$. Equation (2) is easily solved to obtain

$$\phi(\mathbf{x}) = c_1(\mathbf{k})\exp(i\mathbf{k}\cdot\mathbf{x}) + c_2(\mathbf{k})\exp(-i\mathbf{k}\cdot\mathbf{x})$$

and

$$\lambda(k) = -M\hat{\Gamma}[R^2k^2 - |r_0| + 12u\psi_0^2], \quad (3)$$

where $-|r_0| + 12u\psi_0^2$ is assumed to be negative, $k = |\mathbf{k}|$, and Eq. (3) is the eigenvalue for model A (B) if $\hat{\Gamma}=1$ (k^2). The Fourier transforms of $c_1(\mathbf{k})$ and $c_2(\mathbf{k})$ into position space describe the Gaussian initial fluctuation at $t=0$. I have not included the Cook[1] term explicitly since I am not interested in the spatial structure associated with the system at $t=0$ but in the structure evolving due to the instability described by the Cahn-Hilliard equation (1). For this reason the $c(\mathbf{k})$ are arbitrary and will be chosen to be independent of $\mathbf{k}$. With these considerations,

$$u(\mathbf{x},t) \propto \int d\mathbf{k}\exp(i\mathbf{k}\cdot\mathbf{x})\exp[\lambda(k)t],$$

where $\lambda(k)$ is given by Eq. (3) and the fact that $\lambda(k)$ is an even function of k has been used.

This solution can be analyzed for $t\sim 0$ and for large t. What is meant by large will be discussed in greater detail below. The conclusions based on the analysis of these two limits can be simply verified by explicit calculation in model A. I outline the calculations in $d=2$ and 3 and quote results in higher dimensions.

For $t \ll 1$ we can expand $e^{\lambda(k)t}$ in a power series. Keeping only the linear term it is simple to show that for $t \ll 1$, $u(\mathbf{x},t)$ is localized. In the limit $t \gg 1$ we can evaluate the integral using the steepest-descent method.

If k_0 is the value of k that maximizes the right-hand side of Eq. (3), $u(\mathbf{x},t)\sim\sqrt{1/t}\int d\Omega\, e^{i\mathbf{k}_0\cdot\mathbf{x}}$, where the integral is over the direction of $\mathbf{k}_0$.

For model A, $k_0=0$ so that $u(\mathbf{x},t)$ is a spatial constant. This implies a fractal dimension of d, the spatial dimension. For model B, k_0 is not zero and the spatial dependence of $u(\mathbf{x},t)$ is $J_0(k_0x)$ the Bessel function of order zero in two dimensions and $j_0(k_0x)$ the spherical Bessel function of order zero in three dimensions. The asymptotic form of $J_0(k_0x)\sim\cos(k_0x)/\sqrt{k_0x}$ and $j_0(k_0x)=\sin(k_0x)/k_0x$, where $x=|\mathbf{x}|$. Since these functions describe a density variation, d_f can be obtained by noting that the density will scale as $1/x^{d-d_f}$. Therefore, $d_f=1.5$ in $d=2$ and 2 in $d=3$. From the expression for $u(\mathbf{x},t)$ the fractal dimension will clearly remain equal to 2 for $d>3$ implying that 3 is an upper critical dimension. The fractal dimension of 1.5 in $d=2$ is consistent with the measurement in Ref. 2.

Before discussing the multifractality of these structures it should be noted that there is a natural length scale associated with spinodal decomposition and continuous ordering. The steepest-descent evaluation of the integral can only be performed if the $\exp(i\mathbf{k}\cdot\mathbf{x})$ in the expression for $u(\mathbf{x},t)$ is smooth. This implies that $\mathbf{k}\cdot\mathbf{x}\approx 1$. For large values of x this will not be true. An estimate of the largest value of x can be obtained by noting that the Gaussian part of the steepest descent will essentially limit contributions when $(k-k_0)^2t>1$. We require then that $\mathbf{k}_0\cdot\mathbf{x}-(\mathbf{k}-\mathbf{k}_0)\cdot\mathbf{x}$ be constant until $(k-k_0)^2t\sim 1$. This implies that the front of the developing fractal structure is at $x\sim\sqrt{t}$. For x larger than this value it is simple to show that the spatial part of $u(\mathbf{x},t)$ decays exponentially.[8] It is important to note that the structures described here evolve via the linear theory which will only be valid for times[9] in spinodal decomposition less than $R^2\ln R$. Taken together, these considerations imply that the fractal structure extends only over the region of scaled length $x/R\sim\sqrt{\ln R}$.

In order to obtain the multifractal structure we slightly modify the concept of a mass fractal introduced by Vicsek.[10] From the discussion above, in $d=3$ there is a density change at the point x given by

$$\Delta m=\sin(k_0x)/k_0x\,. \tag{4}$$

Imagine now that we cover our system with blocks of linear dimension l and ask how many blocks have a density change of Δm. From Eq. (4) it is relatively easy to see that the number of such blocks is $N(\Delta m)\sim|\Delta m|^{-d}$. This power-law behavior in the density implies a multiscaling behavior. In order to see this explicitly I define a "mass index"

$$\alpha=\frac{\ln(1/|\Delta m|^d L^{d_f})}{\ln(l/L)}\,, \tag{5}$$

where $L\sim\sqrt{t}$ is the linear dimension of the fractal and it is assumed that $L\gg l$.

From Eqs. (4) and (5) it follows that the number of boxes with mass index α, $N(\alpha)$, goes as[10] $L^{f(\alpha)}$ and

$$N(\alpha)\sim L^{d_f-\alpha}\,, \tag{6}$$

where we have set $l=1$. In $d=3$, $d_f=2$ so that $f(\alpha)=2-\alpha$. Note that $f(\alpha)$ can be zero which corresponds to regions of relatively large mass change. Although these large-mass-change regions are rare, they cannot be ignored. This will become clear as we discuss the generalized dimensions D_q, which are defined through the relation[10]

$$\left(\frac{l}{L}\right)^{(q-1)D_q}=\frac{2\ln(L/l)}{(L/l)^{qd_f}}\int_{\alpha_{\min}}^{\alpha_{\max}}d\alpha\left(\frac{l}{L}\right)^{q\alpha-f(\alpha)}\,. \tag{7}$$

The α-independent constant on the right-hand side is a factor that guarantees[10] $D_0=d_f$ and that the $q=1$ moment equals 1 up to order L^{-1}. In order to calculate D_q we need to know the upper and lower bounds for α, $\alpha_{\max}$, and $\alpha_{\min}$. Since $|\Delta m|^d$ is bounded from above by 1, from Eq. (5), $\alpha_{\max}\sim d_f$. The value for $\alpha_{\min}$ is obtained by noting that $|\Delta m|^d L^{d_f}$ is the total mass of the fractal divided by the number of boxes with the same mass. Since this ratio is bounded from below by 1, $\alpha_{\min}=0$ in $d=3$. With $\alpha_{\min}=0$ the maximum value of $f(\alpha)$ is 2, which is equal to d_f as required.[10,11]

In $d=3$, Eq. (7) implies that

$$\left(\frac{l}{L}\right)^{(q-1)D_q}=\frac{2(L/l)^{2-2q}}{q+1}\left[1-\left(\frac{l}{L}\right)^{2(q+1)}\right]. \tag{8}$$

For $q\geq -1$, Eq. (8) implies that $D_q=d_f=2$ as if the structure were a uniform fractal.[11] For $q<-1$, however, $D_q=4q/(q-1)$.

In $d=2$ the asymptotic form of the solution of Eq. (2), $J_0(k_0x)\sim\cos(k_0x)/\sqrt{k_0x}$, results in $N(\Delta m)\sim 1/(\Delta m)^{2d}$. The same arguments as in $d=3$ result in $f(\alpha)=2(1.5-\alpha)$, $\alpha_{\min}=0.75$, $\alpha_{\max}=d_f=1.5$, and $D_q=d_f=1.5$ for $q\geq -2$ and $2.25q/(q-1)$ for $q<-2$. Similar results are obtained for $d>3$ and will be reported elsewhere.[8] The simple multifractal structure obtained in the linear regime of spinodal decomposition is a result of there being only two relevant lengths, L and k_0^{-1}. Model A of course has an even simpler structure, i.e., $D_q=d$ for all q.

Finally, I will discuss the mapping of the early stage of spinodal decomposition and continuous ordering on to a percolation problem, or, more precisely, a cluster growth problem. Without such a mapping it is presently very difficult to measure the fractal and multifractal structures described above with computer-simulation techniques. I begin with the dilute s state Potts model which has been used to map thermal critical points[12,13] and spinodals[14,15] onto percolation transitions. The Hamiltoni-

an is[12]

$$-\beta H = J\sum_{ij}(\delta_{\sigma_i\sigma_j}-1)[n_in_j+(1-n_i)(1-n_j)]+H\sum_i(1-\delta_{1\sigma_i})n_i$$
$$+H\sum_i(1-\delta_{2\sigma_i})(1-n_i)+K\sum_{ij}[n_in_j+(1-n_i)(1-n_j)]-\sum_i\Delta_1n_i-\sum_i\Delta_2(1-n_i)\,, \tag{9}$$

where the sums are over all pairs of spins with separations less than or equal to the interaction range R. The n_i are either 0 or 1, K is the lattice-gas interaction, H is the Potts magnetic field, J is the Potts interaction, and Δ is the chemical potential of spin up (1) or spin down (2). The σ_i specify the direction of the Potts spins and $\delta_{\sigma_i\sigma_j}$ is the Kronecker delta. The derivative of the free energy obtained from the Hamiltonian in Eq. (9) with respect to s and taking the limit $s\rightarrow 1$ produces the generating function for a percolation model[12] where the sites are occupied with up or down spins and bonds are placed at random with the probability $p_b=1-e^{-J}$ between neighboring (i.e., within R of each other) spins in the same direction.

Following a procedure similar to that in Ref. 13 the continuum version of the free energy of this model in the mean-field ($R\rightarrow\infty$) limit can be written as

$$F(\phi,\psi)=\int d\mathbf{x}\left[\frac{1}{2}s(s-1)[R\nabla\phi(\mathbf{x})]^2-\frac{\tilde{r}_1}{2}s(s-1)\phi^2(\mathbf{x})-H(s-1)\phi(\mathbf{x})\right.$$
$$\left.+\frac{\tilde{w}_1}{4!}s(s-1)(s-2)(s-3)\phi^4(\mathbf{x})+\frac{\tilde{w}_2}{2}s(s-1)\phi^2(\mathbf{x})\psi(\mathbf{x})\right]+F_{LG}(\psi)\,, \tag{10}$$

where

$$F_{LG}(\psi)=\int d\mathbf{x}\,\tfrac{1}{2}[R\nabla\psi(\mathbf{x})]^2-\tfrac{1}{2}r_0\psi^2(\mathbf{x})+u\psi^4(\mathbf{x})-h\psi(\mathbf{x})\,. \tag{11}$$

The external field h is proportional to $\Delta_1-\Delta_2$. The constants r_0, $\tilde{r}_1$, $\tilde{w}_1$, $\tilde{w}_2$, and u can be written as functions of J and K and the lattice coordination number c. The essential point is that in this formulation the percolation order parameter $\phi(\mathbf{x})$ is the difference between the probability $\phi_+(\mathbf{x})$ that a spin at $\mathbf{x}$ belongs to the up infinite cluster and $\phi_-(\mathbf{x})$ that a spin at $\mathbf{x}$ belongs to the down infinite cluster. That is, $\phi(\mathbf{x})=\phi_+(\mathbf{x})-\phi_-(\mathbf{x})$. As in the discreet case, the generating function for the percolation model is obtained by differentiating F with respect to s and setting $s=1$.

In order to map the static thermal problem onto the percolation problem we must compare the functional derivative of $dF(\phi,\psi)/ds|_{s=1}=F_P$ with respect to ϕ with the functional derivative of F_{LG} with respect to ψ; i.e.,

$$\frac{\delta F_P}{\delta\phi}=-R^2\nabla^2\phi(\mathbf{x})-\tilde{r}_1\phi(\mathbf{x})+2\frac{\tilde{w}_1}{3!}\phi^3(\mathbf{x})$$
$$+\tilde{w}_2\phi(\mathbf{x})\psi(\mathbf{x})-H \tag{12}$$

and

$$\frac{\delta F_{LG}}{\delta\psi}=-R^2\nabla^2\psi(\mathbf{x})-r_0\psi(\mathbf{x})+4u\psi^3(\mathbf{x})-h\,. \tag{13}$$

In order to have Eqs. (12) and (13) the same we must identify H with h, $2\tilde{w}_1/3!$ with $4u$, and $\tilde{r}_1-\tilde{w}_2\psi(\mathbf{x})$ with r_0. With these choices, the solutions of Eqs. (12) and (13) with $\delta F_P/\delta\phi=\delta F_{LG}/\delta\psi=0$ are identical. Writing these parameters in terms of J, K, and c we obtain the condition $J=2K(1-\rho)$, where the density $\rho=1+m$ and m is the magnetization per spin. This is the symmetrized version of the mapping derived in Ref. 14 which has been used extensively to identify spinodals and critical droplets near spinodals.[15,16]

The interpretation of this mapping is that the spinodal curve is the locus of a set of percolation transitions. If one approaches the curve along the line $\rho=\frac{1}{2}$ (i.e., through the critical point), there is a transition from zero spanning clusters to two, one up and one down at the critical point. If the spinodal curve is approached off critical, there is a transition from one spanning cluster, up or down depending on whether ρ is larger or smaller than $\frac{1}{2}$, to two spanning clusters, one up and one down. The probability that a spin at $\mathbf{x}$ belongs to the up [down] spanning cluster is given by $\phi_+(\mathbf{x})$ [$\phi_-(\mathbf{x})$] and the magnetization is proportional to $\int\phi(\mathbf{x})$. The region in which a mean-field system undergoes spinodal decomposition or continuous ordering is characterized geometrically at time $t=0$ by the existence of two spanning clusters, rather than the existence of one (or none) which geometrically characterizes either the stable or metastable state. We are assuming that the quench rate is fast compared to $R^2\ln R$, the duration of the linear regime.[8]

In order to extend this mapping to spinodal decomposition or continuous ordering we write the equation for the evolution of the order parameter $\phi(\mathbf{x},t)$ for the dilute s-state Potts model in the form $(s-1)\partial\phi(\mathbf{x},t)/\partial t=-M\Gamma\delta F(\phi,\psi)/\delta\phi$. The quantities M and Γ are as defined in Eq. (1) and $F(\phi,\psi)$ is given by Eq. (10). Differentiating both sides of this equation with respect to s, setting $s=1$, and identifying H with h, $2\tilde{w}_1/3!$ with $4u$, and $\tilde{r}_1-\tilde{w}_2\psi(\mathbf{x})$ with r_0 as above, we obtain an equation identical to Eq. (1). In the linear regime of,

e.g., spinodal decomposition where the order parameter in Eq. (1) equals a constant ψ_0 plus a *small* perturbation $u(\mathbf{x},t)$, the Potts interaction J that appears in the bond probability can still be identified[8] as $J=2K(1-\rho)$.

From this result the growing domain in continuous ordering or spinodal decomposition can be associated with a growing cluster formed by throwing bonds at random with a probability $p_B=1-\exp[-2K(1-\rho)]$ between spins in the same direction which are closer together than R. In a Monte Carlo simulation this would correspond to a Metropolis (model A) or Kawasaki (model B) algorithm run on the spins with no notice of the bonds and a bond update after some (arbitrary) number of Monte Carlo steps. It should be noted that the cluster generated by this method indicates the *change* in the cluster structure of the spanning clusters present at $t=0$. Simulations using this mapping to elucidate the fractal structure are currently in progress.[17]

In conclusion, I have identified the fractal and multifractal structure in the early stage of spinodal decomposition in systems with long-range interactions. This structure should be observable in systems with moderate-range interactions for early times.[9] No comparable structure exists for continuous ordering. The fractal dimension in $d=2$ of 1.5 is consistent with the results of Ref. 2.

Of particular interest is the q-dependent dimensions D_q in spinodal decomposition. For $q>0$, D_q is independent of q indicating a uniform structure. However, for $q<q_c<0$, where q_c depends on d, D_q has a structure indicating a second important length. These results pertain to linear theory. One could take the point of view that the $q<-1$ moments are not physical since they have zero probability as $L\rightarrow\infty$ and hence the fractal is uniform. However, for large but finite L the nonlinear theory is valid at later times[1,9] and the negative q moments will mix with the positive ones. This may be responsible for the rich structure seen in spinodal decomposition but not in continuous ordering at later times. It is possible that these low-probability negative moment structures, which are the physical result of the conservation laws, are the reason that perturbation expansions about the linear theory fail.

I would like to thank P. Alstrom, A. Coniglio, H. Gould, M. Hetherington, J. Stringer, and P. Tamayo for useful comments. I would also like to acknowledge the support of the ONR.

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