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Structure and the Failure of the Linear Theory of Continuous Ordering

N. Gross,[1,2] W. Klein,[1,2] and K. Ludwig[1]

[1]*Physics Department, Boston University, Boston, Massachusetts 02215*
[2]*Center for Polymer Physics, Boston University, Boston, Massachusetts 02215*
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We present the results of numerical investigations of Ising models undergoing continuous ordering which indicate, for systems with large but finite interaction range R, that the time interval during which the linear theory of Cahn, Hilliard, and Cook fits the simulation data depends strongly on the length scale of observation. We associate the initial linear theory deviation at small length scales with the appearance of isolated structures or domains which form after a quench into the unstable region of thermodynamic space. These domains cannot be described by a linear theory; this implies, in contrast to earlier results, that the linear theory "breakdown" cannot be obtained by investigation of the linear itself for inconsistencies.

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Spinodal decomposition (SD) [1] and continuous ordering (CO) are the processes by which systems quenched into unstable regions of thermodynamic space begin the evolution to equilibrium. The (CO) SD process describes the evolution in systems in which the order parameter is (not) conserved. These processes are paradigms for understanding many aspects of nonlinear evolution, and information about the underlying mechanisms will not only be valuable to material scientists but will aid considerably in understanding similar processes in several fields.

The first theory to describe these processes was the linear theory of Cahn, Hilliard, and Cook (CHC) [2–4], which begins with the nonlinear Langevin equation [5]

$$\frac{\partial\phi(\mathbf{x},t)}{\partial t} - M\Gamma[-R^2\nabla^2\phi(\mathbf{x},t) + 2\epsilon\phi(\mathbf{x},t) + 4\phi^3(\mathbf{x},t) - h] = \tilde{\eta}(\mathbf{x},t)\,. \quad (1)$$

In Eq. (1) M is a mobility, assumed to be constant, $\Gamma = -1$ for CO and ∇^2 for SD, R is the interaction range, $\phi(\mathbf{x},t)$ is the coarse-grained order parameter, and h is an applied field. The Gaussian noise satisfies $\langle\tilde{\eta}(\mathbf{x},t)\rangle = 0$ and, since all lengths must be scaled by R^{-1}, $\langle\tilde{\eta}(\mathbf{x}/R,t)\tilde{\eta}(\mathbf{x}'/R,t')\rangle = (k_BT/R^d)\delta(\mathbf{x}-\mathbf{x}'/R)\delta(t-t')$, where k_B is Boltzmann's constant and T is the temperature. The delta function must scale as R^{-d} in order to be normalized, which implies that $\tilde{\eta}(\mathbf{x},t) = \eta(\mathbf{x}/R,t)/R^{d/2}$. Equation (1) is linearized by assuming $\phi(\mathbf{x},t) = \phi_0(t) + u(\mathbf{x}/R,t)/R^{d/2}$ where $\phi_0(t)$ is, in general, a function of time and $u(\mathbf{x}/R,t)/R^{d/2}$ is assumed to be small. If we consider a critical quench for simplicity, then $\phi_0(t) = 0$, $h = 0$, and the linearized form of Eq. (1) is

$$\frac{\partial u(\mathbf{x}/R,t)}{\partial t} - M\Gamma[-R^2\nabla^2 u(\mathbf{x}/R,t) - 2|\epsilon|u(\mathbf{x}/R,t)] = \eta(\mathbf{x}/R,t)\,, \quad (2)$$

where we have assumed that $\epsilon(T-T_c)/T_c < 0$. In this Letter we will restrict our discussion to CO but these considerations also apply [6] to SD. Setting $\Gamma = -1$ and $M = 1$, we obtain for $u(\mathbf{x}/R,t)$

$$\frac{u(\mathbf{x}/R,t)}{R^{d/2}} = \int d\mathbf{x}'\frac{u_0(\mathbf{x}'/R)}{R^{d/2}}\exp\left[2|\epsilon|\,t - \frac{|\mathbf{x}-\mathbf{x}'|^2}{R^2t}\right] + \frac{D}{(\sqrt{t})^d}\int d\mathbf{x}\int_0^t dt'\exp\left[2|\epsilon|\,(t-t') - \frac{|\mathbf{x}-\mathbf{x}'|^2}{R^2(t-t')}\right]\frac{\eta(\mathbf{x}/R,t')}{R^{d/2}}\,, \quad (3)$$

where D is a constant that depends on d, and $u_0(\mathbf{x}'/R)/R^d$ is the order parameter at the quench. The structure factor is obtained from Eq. (3) by Fourier transforming the ensemble average $\langle u(\mathbf{x}/R,t)u(\mathbf{x}'/R,t')\rangle/R^d$ with respect to $\mathbf{x}-\mathbf{x}'$.

From Eq. (3) it is clear that the assumption that $u(\mathbf{x}/R,t)/R^{d/2}$ is small cannot be valid for all time. Indeed, Binder using a Ginzburg criterion [7] has pointed out that the time interval during which CHC is self-consistent should scale with the interaction range as $\log R$.

Clearly the linear theory is never exact. However, the proposal that it might be a reasonable fit for the structure factor data for time intervals that scaled as $\log R$ has been tested via Monte Carlo simulation [8,9] and experimentally [10,11] with some success. There are some experimental indications though that the initial deviations of the data from the predictions of the linear theory appear [12] at large $|\mathbf{k}|$, which earlier simulations did not probe. The importance of this observation is that it has implications for the early evolution of real-space structures, and these structures may have an important effect on both materials properties and subsequent nonlinear evolution.

In order to investigate the "breakdown" of the linear theory, particularly for large $|\mathbf{k}|$, we have carried out a series of simulations of two-dimensional Ising models with long-range interactions. In these simulations we have correlated the breakdown of the linear theory with the appearance of isolated structures that initiate the evolution of unstable growth. We find, in contrast to the result in Refs. [7–9] that the linear theory has no time scale over which it fits the data over the entire range of $|\mathbf{k}|$ and that the larger the value of $|\mathbf{k}|$ the earlier the structure factor deviates from the prediction of the linear theory.

Our initial investigations centered on a careful study of the breakdown time for systems quenched from infinite temperature. We measured the structure factor, averaged over 48 realizations, in two-dimensional Ising models with interaction ranges of 7 and 15. Using a Metropolis algorithm we equilibrate the system at $T=\infty$. At time $t=0$ we instantaneously quench to $\frac{2}{3}T_c$ and compare the measured structure factor with the one obtained from the solution of Eq. (2), for several values of the wave number $|\mathbf{k}| = 2\pi nR/L$, where L is the linear system size, and n is an integer. We note the time at which the predictions of the linear theory are outside of the error bars of the measured structure factor. In Fig. 1 we plot the breakdown time t_b vs nR. As can be seen from the figure, the time of deviation from the linear theory remains essentially flat for small $|\mathbf{k}|$ but above some critical value t_b decreases with increasing n. This is consistent with the experimental indications [12].

In order to understand what these results imply about structure we used the fact that the linear theory of SD and CO can be mapped onto a cluster growth model [13]. In the long-range Ising models we have simulated

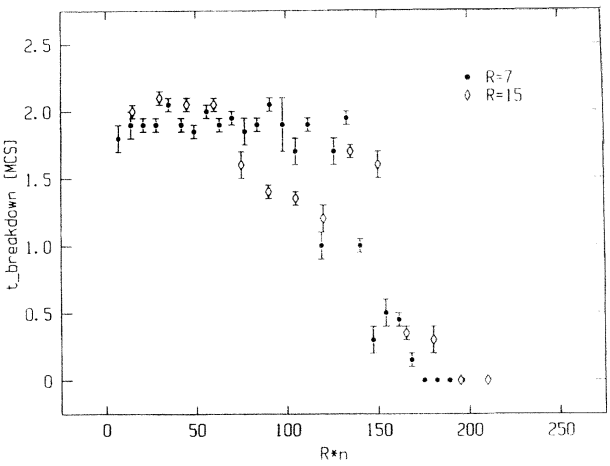

FIG. 1. The time t_b that the structure factor data deviates from the fit to the linear theory as a function of nR, where $|\mathbf{k}| = 2\pi nR/L$, and $L = 512$ is the linear system size.

that this mapping takes the form of randomly assigning a bond with a probability $p_b = 1 - \exp(-2K)$ [here $K = J/k_BTq$, J is the Ising coupling constant, and $q = (2R+1)^d$], between spins of the same sign that are separated by a distance less than the interaction range R.

With this cluster definition, the critical point of the ϕ^4 theory in Eq. (1) is also a percolation transition [13]. For critical quenches, the *cluster* configuration changes from no infinite clusters above the critical temperature T_c to two infinite clusters, one up and one down, below T_c. These clusters are highly interpenetrating, and we stress that this picture is only valid for large R, hence, mean field. Moreover, the percolation transition occurs at the time of the quench when the spin configurations are those associated with the system in equilibrium prior to the quench, while the bond probability uses the temperature to which the system is quenched. These percolation transitions have been found numerically and will be described in detail in a future publication [14].

We use this mapping to investigate the structure. The simulations proceed as follows. As before, we equilibrate an Ising model with interaction range $R \gg 1$ at $T=\infty$, using a Metropolis algorithm. At $t=0$ we lower the temperature to $T=\frac{2}{3}T_c$. Between each update of the Ising spins we place bonds at random with the probability p_b, given above, and measure the cluster properties. We repeat the random bond distribution N times between spin updates.

The primary variable we measure is $f_I(\mathbf{x},t)$, the fraction of N bond realizations for a fixed spin configuration that the spin at $\mathbf{x}$ belongs to either infinite cluster. At the quench time $t=0$, $f_I(\mathbf{x},0)$ is a spatial constant. As the spins are updated and the system begins to evolve, isolated regions of increased $f_I(\mathbf{x},t)$ emerge, i.e., regions with increased probability of belonging to

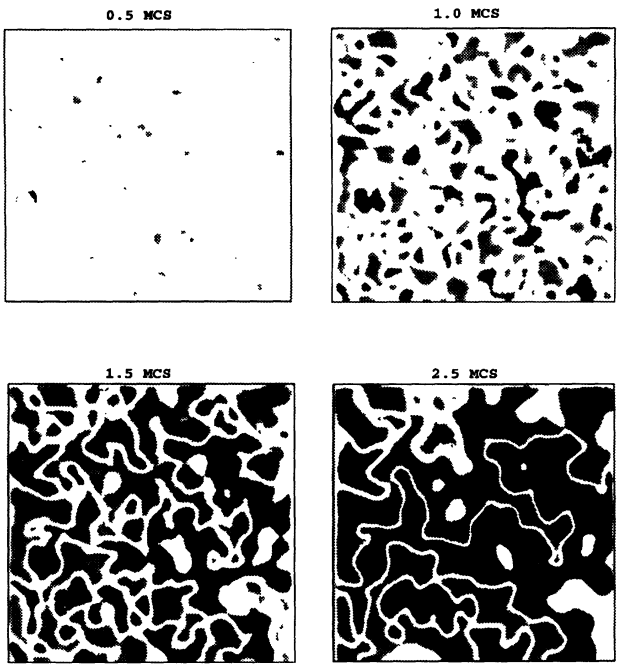

FIG. 2. Isolated regions of enhanced probability of belonging to the up or down infinite cluster. The system size $L = 512$, and the interaction range $R = 7$. At $t = 0.5$ MCS, there are only isolated domains. At $t = 1$ MCS, the domains have begun to coalesce. At $t = 1.5$, the domains have not percolated, while at $t = 2.5$ they have. At $t = 2$ (not shown), the domains have almost percolated in this run if we demand that percolation is a connected cluster that spans the system.

an infinite cluster, or equivalently, regions of increased magnetization. Until $f_I(\mathbf{x}, t)$ in these regions exceed a threshold of order $R^{-d/2}$ they are not unstable domains but are "equilibrium fluctuations" (see below). Hence, our domains are regions of $f_I(\mathbf{x}, t)$ that exceed a threshold of order $R^{-d/2}$. Figure 2 shows several of these enhanced probability areas at various times after the quench for an Ising model with interaction range R quenched from $T = \infty$ to $T = \frac{2}{3}T_c$. These are also regions of increased density of either up or down spins.

White areas indicate the absence of fluctuations which exceed threshold (see below). Black (grey) indicates an enhanced probability of belonging to the up (down) infinite cluster. The time evolution of $f_I(\mathbf{x}, t)$ indicates an increasing probability of belonging to the infinite cluster. We have measured the diameter of the domains when they first appear, and they are approximately the size of the correlation length $\xi = R\epsilon^{-1/2}$.

To get a better understanding of these enhanced domains and the threshold we can view the expression for $u(\mathbf{x}/R, t)/R^{d/2}$ in Eq. (3) as describing localized regions whose distribution is governed by the Gaussian noise. These regions are isolated for some time because the instability in Eq. (1) and (2) can only amplify fluctuations greater than a certain threshold. This conclusion follows from the observation that after the quench the system is at the top of a maximum in the Landau-Ginzburg free energy. In order for the instability to kick in, the system must "know" that it is at a maximum rather than at a minimum. This requires that a fluctuation of the linear dimension of the equilibrium correlation length ξ have an order-parameter change whose square is greater than the susceptibly. This leads to a criterion similar to the standard Ginzburg criterion, i.e., $u^2 \sim \chi_T/\xi^d$ or $u \sim |\epsilon|^{(d-2)/4}/R^{d/2}$. Here u is the order-parameter density in a domain. Also note the scaling with $R^{-d/2}$ consistent with $\tilde{\eta}(\mathbf{x}, t)$ in Eq. (2). In $d = 2$, $u \sim 1/R$ is the threshold below which fluctuations are still in "equilibrium." Clearly $u \to 0$ as $R \to \infty$.

Using the idea that fluctuations of the magnetization in mean field models can be described as a random walk in order-parameter space [15] with a step size ξ^{-d}, we can estimate (from u^2) the time τ it takes for the domains to begin to interact to be of the order $\tau \sim |\epsilon|^{-1}\xi^d$ in spin flips or $|\epsilon|^{-1}$ in Monte Carlo steps (MCS). Note that this time is independent of R. When the average random walk reaches the threshold magnetization, the system will consist of domains that are close enough to affect each other, and the random walk picture will begin to break down and the domains coalesce. Another prediction that follows from the random walk model is that the initial appearance of the domains can be understood from the dispersion in the random walk. A simple calculation leads to the prediction that for times small compared to τ the number of domains will grow linearly with time.

In Fig. 3 we plot the number of domains as a function of time for three different interaction ranges. Note that the domains are strongly coalescing at $\tau \sim 1$ MCS independent of R, and the initial increase in the number of domains is linear with a slope independent of R.

We make the following observations: (1) During the evolution immediately after the quench isolated domains appear in which the density of up or down spins varies significantly from the initial value of $\frac{1}{2}$. (2) The domain diameter when it first appears is, within numerical error, equal to L/nR at the value of nR (from Fig. 1), corresponding to the $t = 0$ breakdown. (3) From Fig. 1 we can separate the breakdown times t_b into two groups. From $t_b = 0$ until about 2 MCS, the t_b associated with the deviation from the linear theory is related approximately linearly to $|\mathbf{k}|$. Therefore, deviations from the linear theory have only appeared in our analysis for $|\mathbf{k}| > |\mathbf{k}|_{\max}(t)$. At approximately 2 MCS, the entire range $0 \leq |\mathbf{k}| < |\mathbf{k}|_{\max}(t = 2)$ goes nonlinear simultaneously. (4) At about 2 MCS, the growing domains which were previously isolated percolate, providing regions of increased density on all length scales.

We conclude from these observations that the isolated domain structures are the location of the initial evolution

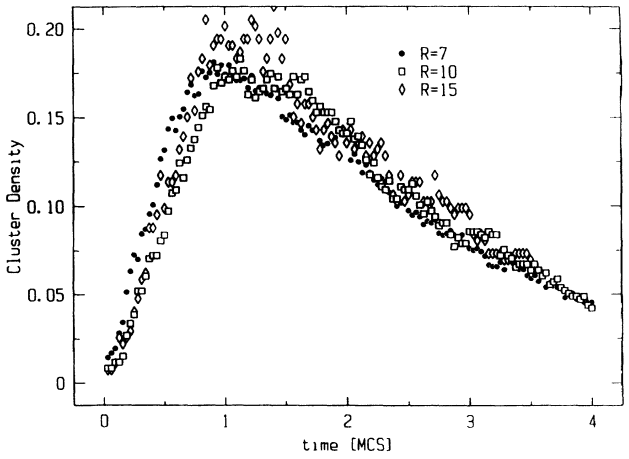

FIG. 3. The density of clusters of enhanced regions as a function of time. The increase is linear and the decrease is due to coalescence. The system size $L = 512$.

away from the linear regime which accounts for the structure factor deviation at large $|\mathbf{k}|$. Moreover, the percolation transition of the domains is responsible for the instantaneous increase in the range of $|\mathbf{k}|$ for which deviation from CHC occurs.

The results also imply that the CHC linear theory has no interval of validity for any finite R, since the isolated domains appear during the initial evolution after the quench and the time they first appear is independent of R (Fig. 3). This result is significantly different from those obtained [7] earlier in two ways. First, it predicts that the linear theory is fundamentally flawed for any time after the quench for finite R. Second, that the time of the initial deviation depends on the length scale, or equivalently, the $|\mathbf{k}|$ vector probed. More precisely, localized domains will form at $t = 0$ inside of which the linear theory no longer applies. From the rather weak dependence of t_b on R for $|\mathbf{k}| < |\mathbf{k}|_{\max}(t = 2)$ (Fig. 1) after the domains have percolated, we speculate that the Ginzburg criterion proposed by Binder [7] applies for this range of $|\mathbf{k}|$.

We stress that this is a new view of the early stage morphology of system undergoing CO and the first connection, to our knowledge, between real-space structure and the breakdown of linear theories. We have performed simulations with spin-exchange dynamics which indicate [6] that the same initial evolution of domains occurs for spinodal decomposition. That is, the early morphology of Ising models with long-range interactions undergoing spinodal decomposition is indistinguishable from that in Fig. 2. In addition, we have investigated the effect on our conclusions of taking into account higher-order derivatives (∇^4, etc.) in the CHC equations [6]. While the fits are better, the same qualitative behavior emerges, i.e., the CHC theory deviates from the data at high wave numbers first.

In conclusion, we have presented a new picture of the morphology of the early stage of evolution in systems quenched into the unstable region of the phase diagram. In addition, we have argued that the CHC theory is not valid for any time after the quench although it may remain a good approximation for small $|\mathbf{k}|$ for $t \sim \log R$, as proposed by Binder. We have also proposed an explanation for the $|\mathbf{k}|$ dependence of t_b seen experimentally. Finally, we believe that the understanding of the linear regime morphology and its relation to the breakdown of CHC will aid in formulating a more complete nonlinear theory than those currently available.

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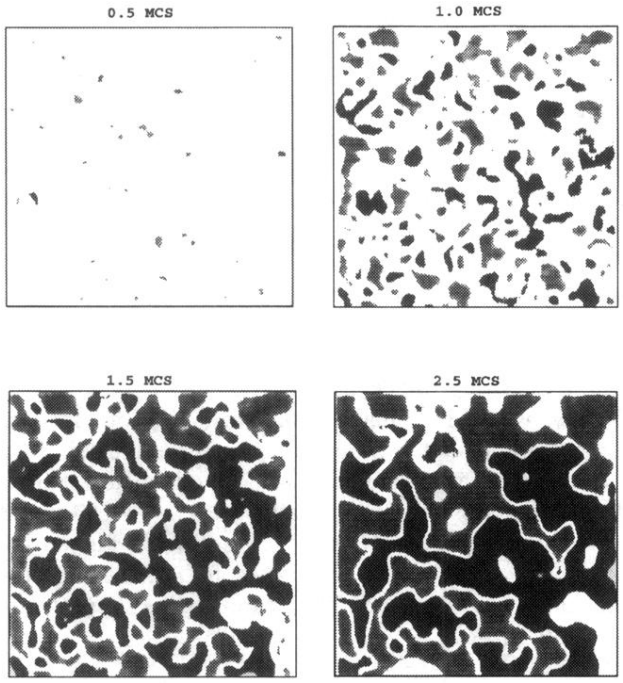

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