RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 39, NUMBER 1 1 JANUARY 1989

Effect of the morphology of patterns on the scaling functions: Off-critical quenches

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(Received 29 September 1988)

We present results of a numerical study of the Cahn-Hilliard model for phase separation for off-critical quenches in two dimensions. We have computed the scattering intensity, the pair correlation function, and the cluster distribution function. We have found that these three quantities can be described in terms of scaling with a time-dependent length and have compared the relevant scaling functions with those obtained in the critical quenches. The time dependence of the characteristic length of the domains is also studied.

In the "classical" theory of the kinetics of first-order phase transitions,[1] a distinction is made between two very different mechanisms of evolution following a quench from a very high temperature to a point within the miscibility gap. If the system is left in the metastable region of the phase diagram (between the so-called spinodal line and the coexistence curve) the system evolves by nucleation and subsequent growth of the nuclei formed. Between the spinodal and the center of the phase diagram, the system is unstable against long-wavelength instabilities and evolves by spinodal decomposition. It is known, however, that the transition from nucleation and growth to spinodal decomposition and coarsening mechanism is not as sharp as described in this theory. Even the meaning of a spinodal curve has been questioned both theoretically and experimentally.[2] However, the interconnected structure, seen in the case of spinodal decomposition, has a very different morphology from that appearing in the "nucleation regime." One of the most relevant questions in the kinetics of first-order phase transitions is the effect of the different morphologies on experimentally relevant measuring probes, such as the scattering intensity. In theoretical studies[3] one finds that the time-independent scaling functions, calculated from the structure factor, depend on the concentration of one of the constituents, at least in three dimensions and in the limit of small volume fractions. The perturbative nature of these studies does not allow an extension to large volume fractions. Also, no such systematic studies are available in two dimensions. Recently, the dynamics[4] of critical quenches in two dimensions have been studied extensively by a variety of numerical methods: Monte Carlo simulation of the Ising model with Kawasaki dynamics, numerical integration of Langevin equations with and without noise,[5,6] and cell dynamics methods.[7,8] These studies have provided reliable data for the scaling functions. At this point, it seems worthwhile to carry out a detailed calculation for off-critical quenches and study the possible effect of the radically different morphology of patterns on the scaling functions.

In this Rapid Communication we report results from a numerical study of the Cahn-Hilliard model[9] in two dimensions for an off-critical quench. We have chosen a value of the (conserved) concentration such that the system is on the mean-field spinodal curve. We have computed the scattering intensity, the pair correlation function, and the cluster distribution function. We have found that these three quantities can be described in terms of scaling with a time-dependent length and have compared the relevant scaling functions with those obtained in the critical quenches. The time dependence of the characteristic length of the domains is also studied and is found to be in agreement with existing theories.

In the Cahn-Hilliard theory, one is concerned with the time variation of a locally defined conserved concentration field, $\psi(r,t)$. It is assumed that the system is driven by a free-energy functional given by the Ginsburg-Landau expression. The resulting equation of motion then can be written as

$$\frac{\partial\psi}{\partial t}=M\nabla^2[-b\psi+u\psi^3-K\nabla^2\psi]+\eta\,, \tag{1}$$

where M is the constant mobility and b, u, and K are phenomenological (positive) coefficients. $\eta(r,t)$ is the thermal noise. Since we are interested in the scaling behavior of the system, the noise term is neglected in Eq. (1), as it has been shown recently that the scaling function does not seem to change with the inclusion of the noise term.[5] This equation can be written in a simple form after rescaling the field $\psi(r,t)$ by its mean-field equilibrium value $\sqrt{b/u}$, the distance by the mean-field correlation length $\sqrt{K/b}$, and the time by $2K/Mb^2$. The resulting parameterless equation is[10]

$$\frac{\partial\psi}{\partial t}=\tfrac{1}{2}\nabla^2(-\nabla^2\psi-\psi+\psi^3)\,. \tag{2}$$

We have numerically integrated Eq. (2) on a square lattice of size 256^2 [in the dimensionless units of Eq. (2)] with periodic boundary conditions. We chose the initial configuration to be a Gaussian distribution centered at $\psi_0=1/\sqrt{3}$ with variance unity. In order to average over initial random configurations, we have performed 40 runs with different initial configurations. We have performed the numerical integration up to $t=20000$ (in the above

mentioned units) using a time step $\delta t = 0.025$ and a mesh size $\delta x = 1.0$. We have found that larger values of δx produce droplets of the minority phase which grow anisotropically. With the choice of $\delta x = 1.0$ we find that the droplets are circular and that the measure of the domain size given by the radius of gyration agrees with the geometrical radius. We have also checked that lower values of δt do not alter the quantities measured.

We now present the main results of this study. In Fig. 1 we present a typical morphology of the system at $t = 20000$. The few droplets seen in this figure have evolved from a situation at much earlier times in which there were many droplets. The big droplets then grew at the expense of the smaller droplets which shrank and then finally disappeared. This situation is very different from what has been seen in numerical studies for critical quenches.[4-6] As is obvious from the figure, the droplets are very circular and it, therefore, makes sense to define a typical domain size as the radius of gyration $R_G(t)$. We have found, however, that a more suitable quantity (from the statistical point of view) is the first zero of the circular average of the pair-correlation function

$$\hat{G}(\mathbf{r},t) = \left\langle \frac{1}{N} \sum_{\mathbf{r}'} [\psi(\mathbf{r}+\mathbf{r}',t)\psi(\mathbf{r},t) - \psi_0^2] \right\rangle . \tag{3}$$

We call this measure $R_g(t)$. $R_g(t)$ and $R_G(t)$ behave qualitatively in the same way and both follow the Lifshitz-Slyozov law.

An important quantity in the description of this kinetic process is the distribution function $n(l,t)$ such that $n(l,t)dl$ gives the number of droplets in the system of sizes between l and $l+dl$ at time t. Here, we have defined a droplet as a simple connected set of sites with a negative value for the field. The size of the cluster is defined as the number of lattice sites that belong to it. Given the fact that the droplets are very large in terms of the lattice spacing, this definition is equivalent to defining the droplet size as the geometrical area. The numerical computation of the function $n(l,t)$ is difficult, because even for a 256^2 lattice the number of droplets at late times is not very large (around 25–30, see Fig. 1). In order to improve statistics we have calculated $n(l,t)$ by counting the number of cluster between sizes $l-\delta l$ and $l+\delta l$. The necessary values of δl to get smooth data need to be increased with time, e.g., $\delta l = 20$, 30, 40, and 50 for $t = 8000$, 12000, 16000, and 20000, respectively.

The Lifshitz-Slyozov theory and other phenomenological scaling theories predict a scaled form for the droplet distribution function of the following form:

$$n(l,t) = \overline{l(t)}^{-2} N\left(\frac{l}{\overline{l(t)}}\right), \tag{4}$$

where $\overline{l(t)}$ is the mean area of the clusters at a given time t. Since $\overline{l(t)} \propto R_g(t)^2$ we have checked this scaling ansatz by plotting $n(l,t)R_g(t)^4$ vs $l/R_g(t)^2$ in Fig. 2. In this figure we see that scaling holds reasonably well at late times.

An experimentally accessible quantity is the structure function, defined as the Fourier transform of the pair correlation function

$$\hat{S}(\mathbf{k},t) = \sum_{\mathbf{r}} e^{i\mathbf{k}\cdot\mathbf{r}} \hat{G}(\mathbf{r},t) . \tag{5}$$

The vector $\mathbf{k}$ belongs to the first Brillouin zone in the reciprocal space. We concentrate on the circularly averaged structure function $\hat{S}(k,t)$:

$$\hat{S}(k,t) = \frac{\sum_{k-\frac{1}{2}\delta k < |\mathbf{k}| \le k+\frac{1}{2}\delta k} \hat{S}(\mathbf{k},t)}{\sum_{k-\frac{1}{2}\delta k < |\mathbf{k}| \le k+\frac{1}{2}\delta k} 1} . \tag{6}$$

The quantity defined in the denominator of Eq. (6) denotes the number of lattice points in a circular shell of width δk, centered around k. Due to the discreteness of the lattice used, $\hat{S}(k,t)$ might depend on δk for small values of k if δk is not small enough.[11] We have used

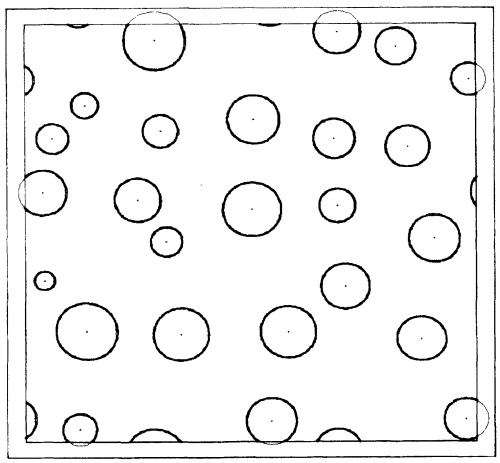

FIG. 1. A typical configuration at $t = 20000$ during the evolution of the system. The number of droplets in this particular case is 25. Note that the droplets are circular in shape as indicated by drawing circles (solid line) with radii equal $\sqrt{2}R_G(t)$ where $R_G(t)$ are the corresponding radii of gyration of the clusters. The part of the circles outside the inner frame indicate images coming from the periodic boundary conditions.

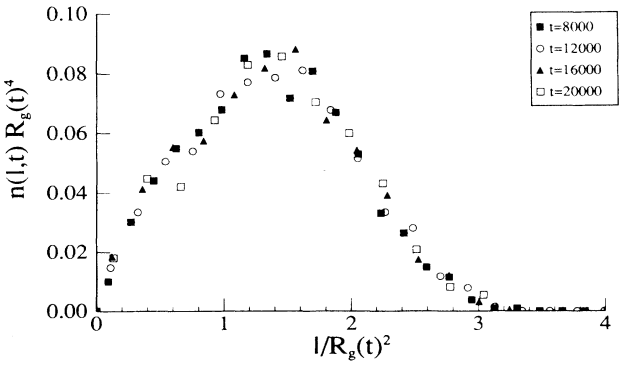

FIG. 2. Scaling plot of the cluster distribution function $n(l,t)$ in order to check scaling ansatz [Eq. (4), see text]. Since the clusters are circular we have used $\overline{l(t)} \propto R_g(t)(t)^2$. Note that the scaling holds reasonably well after $t = 8000$.

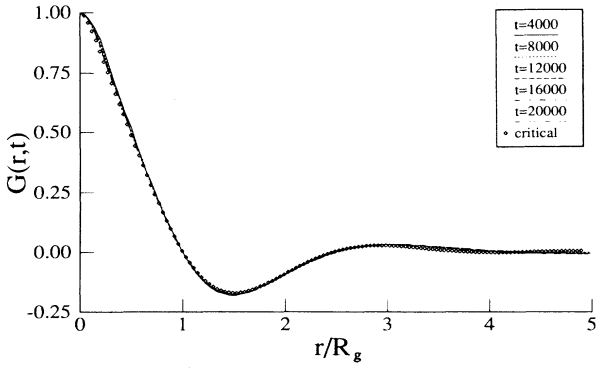

FIG. 3. Plot of the normalized pair-correlation function $G(r,t)$ vs $r/R_g(t)$ to check the scaling ansatz [Eq. (7), see text]. Within the accuracy of the data scaling is well satisfied after $t=4000$. We also include the scaling function derived in a critical quench (Ref. 6).

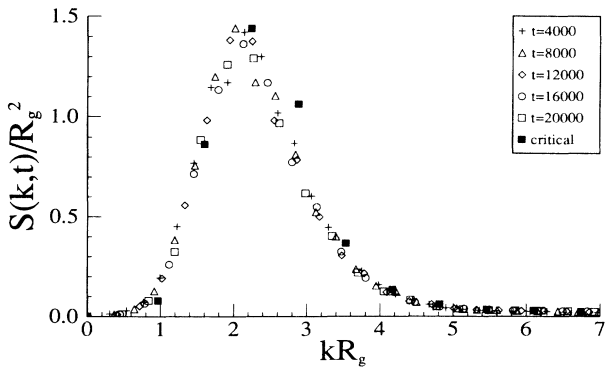

FIG. 4. Plot of the normalized structure factor $S(k,t)$ vs $kR_g(t)$ to check the scaling ansatz [Eq. (8), see text]. Within the accuracy of the data scaling is well satisfied after $t=4000$. We also include the scaling function derived in a critical quench (Ref. 6).

$\delta k=(2\pi/256)\times 0.75$ and $\delta k=(2\pi/256)\times 1.0$ and we have found no appreciable difference in the results.

The dynamical scaling ansatz for the circularly averaged pair correlation function $\hat{G}(r,t)$ states that

$$\hat{G}(r,t)=\hat{G}(0,t)g(r/R_g(t)) . \tag{7}$$

We include $\hat{G}(0,t)$ in this equation because this allows us to compare the scaling function with that computed for critical quenches. In Fig. 3 we plot $G(r,t)\equiv\hat{G}(r,\hat{t})/G(0,t)$ vs $r/R_g(t)$ and show that scaling holds extremely well at times greater than $t=4000$. In the same figure, we include the scaling function for a critical quench.[6] Surprisingly enough, despite the radical differences in morphology, the scaling functions are very close to each other. Similar conclusions are reached when comparing the scaling functions obtained from the structure function.

The dynamic scaling hypothesis for $\hat{S}(k,t)$ is

$$S(k,t)\equiv\frac{\hat{S}(k,t)}{\hat{G}(0,t)}=R_g(t)^2F(kR_g(t)) . \tag{8}$$

Figure 4 shows the comparison of the scaling functions $F(x)$ derived from our numerical study and from studies of critical quenches[6] of the Cahn-Hilliard equation. It is interesting to note that both scaling functions have a similar shape and that the peak is located at the same position. We also note that the off-critical structure functions calculated in a cell-dynamics model[12] also suggest the same qualitative conclusions. It is also pointed out in Ref. 12 that the noise effect becomes important when the off-criticality is increased.

Theoretical calculations by Tokuyama, Enomoto, and Kawasaki[3] show that, in three dimensions and for small volume fractions, the shape of the structure function changes substantially with the volume fraction. One expects that similar qualitative conclusions should apply as well in two dimensions. Our study indicates that the scaling functions for quenches on the mean-field spinodal line and critical quenches are quite similar. However, we should point out that it is numerically very difficult to conclude whether the large-r behavior for the pair-correlation scaling function is indeed independent of the volume fraction. Similar reservations should apply to the structure function for small k values. Even then, it is apparent from this study that even if there are some changes in the scaling functions for these two quenches, the differences are smaller than that seen in the theoretical studies, considering the fact that the volume fraction changes by a factor of 2.5 for these two cases. This might be due to the fact that the detailed quantitative conclusions of the theory are different in two and in three dimensions or that the theory breaks down for the large volume fractions considered here.

We acknowledge E. T. Gawlinski and J. Viñals for providing us with their simulation data. This work was supported by National Science Foundation Grant No. DMR-8612609 and by a National Science Foundation grant of computer time at the Pittsburgh Supercomputing Center. One of us (R.T.) acknowledges financial support from United States/Spain Grant No. CCB-8402/025.

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