Numerical Study of the Cahn-Hilliard Equation in Three Dimensions

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(Received 14 March 1988)

We present results of the first numerical study of the Cahn-Hilliard equation in three dimensions. We study the asymptotic time dependence of the characteristic domain size $R(t)$, as well as the scaling of the pair correlation function and the structure factor. The results indicate that dynamical scaling holds at sufficiently late times and that the data for $R(t)$ are consistent with a Lifshitz-Slyozov growth law $R(t)\sim t^{1/3}$.

PACS numbers: 64.60.My, 02.70.+d, 64.60.Cn

The theoretical understanding of the process of phase separation, which occurs in many binary mixtures after quenching into the miscibility gap, is based mainly on the Cahn-Hilliard formulation.[1] In the Cahn-Hilliard theory, the time variation of the conserved concentration field $\psi(\mathbf{r},t)$ is given in terms of the functional derivative of a time-dependent coarse-grained free-energy functional $F[\{\psi(\mathbf{r},t)\}]$, namely

$$\frac{\partial\psi(\mathbf{r},t)}{\partial t}=M\nabla^2\frac{\delta F}{\delta\psi}, \tag{1}$$

where M is the (constant) mobility and the noise term is neglected. The free-energy functional is assumed to have the Ginzburg-Landau form:

$$F=\tfrac{1}{2}\int d^3r(K|\nabla\psi|^2-b\psi^2+\tfrac{1}{2}u\psi^4), \tag{2}$$

where K, b, and u are positive constants. Substitution of Eq. (2) into Eq. (1) gives a complicated nonlinear partial differential equation for the field $\psi(\mathbf{r},t)$ (the Cahn-Hilliard equation) which is extremely difficult to solve analytically. While there are some approximate theories[2,3] that provide early-time behavior, no systematic analytic study of the late-time behavior of the phase-separation process exists (with the exception of a recent low-temperature expansion[4] which we mention later). It seems at this point that the best method to extract useful information about late-stage growth is numerical integration.

It is interesting to study the dynamics of the system following a quench into the unstable region of the phase diagram. The quench through the point in the unstable region characterized by an equal concentration of the two phases is perhaps the most interesting one because of the intrinsic symmetry of the problem. However, it is difficult to perform a quench at exactly the critical concentration in real materials, in part because for many mixtures the coexistence curve is not well known or is asymmetric. Numerical studies have provided, until now, the only unquestionable critical quenches. To our knowledge, the only three-dimensional studies to date have been that of Lebowitz, Marro, and Kalos,[5] who performed Monte Carlo simulations of the Ising model with conserved order parameter. In their work, the authors studied the dynamics of the system following quenches to various points in the phase diagram. However, no similar study exists for the Cahn-Hilliard equation.

In this Letter we want to fill this gap by presenting results of a detailed numerical study of the Cahn-Hilliard equation in three dimensions. It turns out that the numerical solution of this equation is very demanding in terms of computer resources (both central-processing-unit time and memory). Also, in order to extract statistically reliable information, a larger number of runs in a very large system is necessary. We have carried out the simulations to a very late time and averaged over a reasonably large number of runs. The size of the domains seen in our study implies that we are in late-time regime compared to earlier Monte Carlo studies. Also, the large number of runs provides us with better quality data than that available in the literature. We calculate the pair correlation function and the structure factor, among other quantities, and use them to study dynamical scaling *Ansätze* and the domain growth law.[1,4-6]

The resulting equation after we substitute Eq. (2) into Eq. (1) can be rewritten in a simplier form after suitable rescaling of the field $\psi(\mathbf{r},t)$, the distance, and the time. The resulting parameterless equation is[3]

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

As formulated, this theory is deterministic in nature in the sense that fluctuations are neglected. Thermal fluctuations can be taken into account by addition of a noise term to the right-hand side of Eq. (1). It has been shown,[7] however, that in the late stages of the evolution at low temperatures many essential features are not modified by the inclusion of noise. In particular, the scaling with time of the pair correlation function and the growth law for the typical domain size are not changed by the thermal noise.

We have studied Eq. (3) on a simply cubic geometry

of size 112^3 [in the dimensionless units of Eq. (3)] with periodic boundary conditions by using a grid of 66^3 lattice points. We have performed the numerical integration up to $t=20000$ (also in the above-mentioned units) using a time step $\delta t=0.1$.[8] We chose the initial configuration to be uniformly distributed between -0.125 and 0.125 with order parameter equal to zero (i.e., a critical quench). In order to average over initial random configurations, we have performed 46 runs up to $t=10000$ and 25 runs up to $t=20000$. This is a considerable improvement in the number and length of the runs compared with the previous Monte Carlo studies. As well, our system size is much larger than that used in the Monte Carlo studies. The specific details of the numerical integration will be given elsewhere.[9]

There is now overwhelming evidence that the late stages of the segregation process can be described in terms of scaling with a time-dependent length.[1,5,10,11] The fundamental assumption of the scaling approach to the dynamics is that, in the late stages of the coarsening, only one length, $R(t)$, is relevant. This characteristic length represents a measure of the typical domain size which increases with time. A main feature emerging from this picture of a single relevant length is that the pair correlation function $G(\mathbf{r},t)$ and its Fourier transform, the structure factor $S(\mathbf{k},t)$, depend on time through $R(t)$ only, namely,

$$G(\mathbf{r},t)=g(\mathbf{r}/R(t)) \tag{4}$$

and

$$S(\mathbf{k},t)=R(t)^d F(\mathbf{k}R(t)), \tag{5}$$

where d is the dimensionality of the system. The functions $g(x)$ and $F(x)$ and the growth exponent a define the different dynamical universality classes and their theoretical determination is one of the most challenging problems in the kinetics of first-order phase transitions.

The scaling *Ansatz* (4) has been analyzed in Fig. 1 with use of the spherically averaged correlation function $G(r,t)$. $R(t)$ is defined here as the coordinate of the first zero of $G(r,t)$. This figure seems to indicate that scaling is satisfied for all r, at late times. However, we want to stress that scaling is probably not as perfect as suggested by Fig. 1. A closer look shows that there is a very small but systematic decrease with time of the first minimum of $G(r,t)$. When $t>15000$, however, all the data collapse onto a single master curve (at least, within the precision of the data). On the other hand, the value $G(r=0,t)=0.88$ for $t=20000$ is close to but not equal to the asymptotic (equilibrium) result $G(r=0)=1$, corresponding to the physical situation where we have two homogeneous phases (with $\psi=+1,-1$ as the respective values for the field), separated by sharp interfaces.[12] In that case the ratio of the interface thickness to the domain size tends to zero (a condition necessary for the establishment of the true scaling regime). In order to check this point we studied the probability distribution function $P(\psi,t)$ for the field ψ, which contains information about the interfaces.[13] In the late stages $P(\psi,t)$ consists mainly of two sharp peaks centered at $\psi=-1$ and $+1$, respectively, corresponding to the two coexisting phases, and the values of $P(\psi,t)$ for $\psi\approx 0$ provide the characteristic profile of the interface. By using a hyperbolic tangent form for the interface profile we have been able to determine[9] that the interface thickness is almost a constant in the late stages and that the ratio of the interface thickness to the domain size is of the order of 2% for $t=20000$. While the number is small, it is certainly not equal to zero and, as time goes on, scaling will improve. We believe, though, that the curve given in Fig. 1 is the asymptotic scaling function $g(x)$, excluding small values of x ($x\lesssim 0.3$).

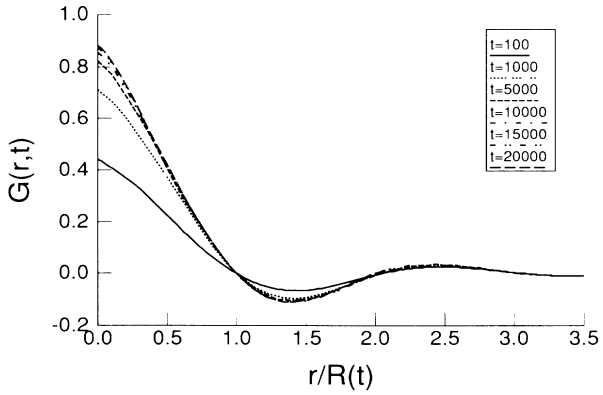

FIG. 1. Scaling function $g(x)$ [Eq. (4)], for the spherical average of the pair correlation function. For sufficiently late time all the data collapse onto a single master curve. The maximum value for r is limited to $\frac{1}{2}$ of the linear dimension of the system because of the periodic boundary conditions.

Figure 2 shows the data for the spherically averaged structure factor $S(k,t)$ plotted to verify the scaling *Ansatz* Eq. (5) with the same measure for the domain size $R(t)$ as in Fig. 1. As shown by the inset, scaling holds extremely well for large values of k. The fact that Eq. (3) is solved on a lattice imposes a discretization in the first Brillouin zone in $\mathbf{k}$ space and restricts the possible values of k, preventing us from studying the scaling *Ansatz* for the structure factor for small values of $k\lesssim k_{\max}$, where $k_{\max}$ denotes the position of the peak $S(k,t)$. Unfortunately, this is part of the experimentally interesting range of k values. Clearly, simulations of much larger samples would be necessary in order to resolve this issue. We believe that this would require substantially more computer resources than is presently available. The present study used about 300 h of Cray model X-MP central-processing-unit time.

We have compared the scaled structure factor with the available Monte Carlo results and recent theoretical predictions. There is a small but significant difference be-

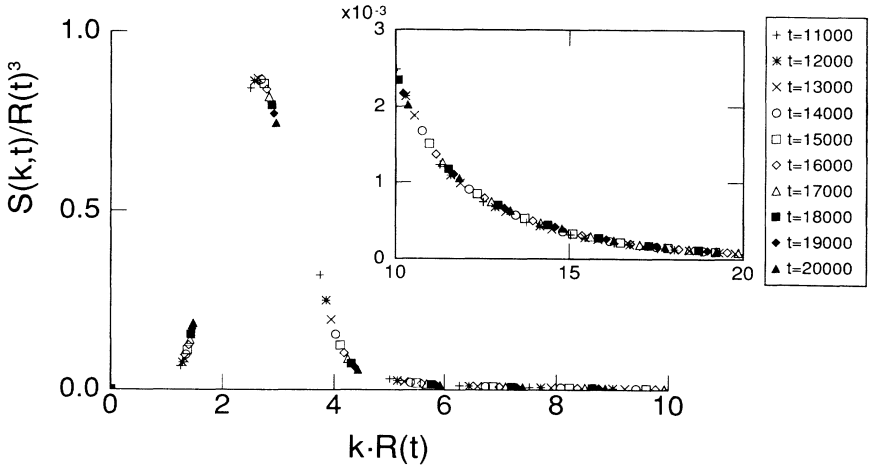

FIG. 2. Scaling function $F(x)$ [Eq. (5)], for the spherically averaged structure factor. As shown by the inset, the scaling is very good for large values of k. For small values of k, the lattice discretization used to solve Eq. (3) prevents us from making a definite statement.

tween the scaling function in Fig. 2 and that obtained in the Monte Carlo studies. This is partly because the Monte Carlo simulation was done in a smaller system and probably did not reach the asymptotic scaling regime. Also, neither the phenomenological form described in Ref. 11, nor the one predicted in Ref. 4 are consistent with the scaling function of Fig. 2.

The characteristic length scale $R(t)$ is expected to behave as t^a for sufficiently late time t. The Lifshitz-Slyozov theory, based on a mechanism of evolution governed by bulk diffusion across the interfaces, has been qualitatively extended by Huse[6] to the case of equal volume fraction of the two phases with the prediction that $dR/dt = AR^{-2} + BR^{-3}$, which translates into a late-time behavior $R(t) \approx B + At^{1/3}$. This is equivalent to one's saying that the effective exponent defined as

$$a_{\text{eff}}(t) = \frac{d\ln R(t)}{d\ln t} = \frac{1}{3}\left[1 - \frac{B}{R(t)}\right]$$

approaches asymptotically $a = \frac{1}{3}$. On the other hand, a recent theoretical study of the dynamics[4,14] (combined with numerical simulations) predicts that, for a critical quench, the effective exponent approaches $a = \frac{1}{4}$ from below for both two and three dimensions. For two-dimensional systems, recent numerical studies of the Cahn-Hilliard equation with and without thermal noise,[7,15] the kinetic Ising model with Kawasaki dynamics,[16] and a cell-dynamics approach[17,18] all yield $a = \frac{1}{3}$ and suggest that these models actually belong to the same dynamical universality class.[19] In three dimensions, the situation is not so clear. Experimentalists have been analyzing their data in terms of effective exponents which lie in the range 0.15–0.37.[1,20] In the Monte Carlo studies of the kinetic Ising model, the authors interpreted their results for the domain size in terms of an effective exponent in the range 0.19–0.35, the smaller exponents corresponding to the critical quenches, although the authors claimed that the data are always compatible with $a = \frac{1}{3}$.

Figure 3 shows our results concerning the time evolution of the domain size $R(t)$. We have used two different but closely related measures of the characteristic length $R(t)$: $R_1(t)$ defined as the coordinate of the first zero of the spherically averaged correlation function $G(r,t)$ and $R_2(t)$ defined as the coordinate of the first zero of the correlation function averaged along the lattice axes. The data for $R_1(t)$, even though containing less statistical errors, have an intrinsic error comparable to the bin size used in the sphericalization. For this reason we believe that $R_2(t)$ provides a more accurate measure of the domain size. Although it is, of course, difficult to distinguish between exponents $\frac{1}{3}$ and $\frac{1}{4}$ since their difference is small, two alternative ways of our

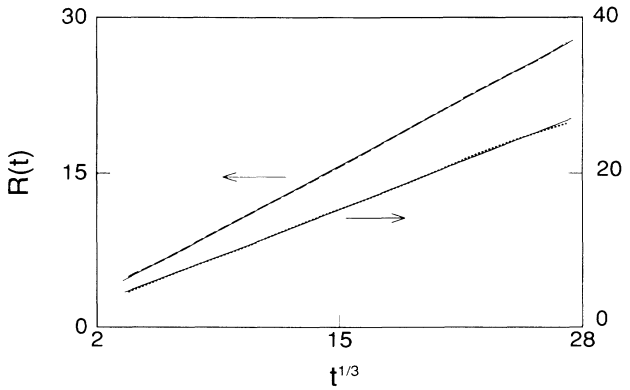

FIG. 3. Time evolution of the characteristic domain size $R_1(t)$ (dotted line), and $R_2(t)$ (dashed line) defined in the text, vs $t^{1/3}$. The straight lines are the best fits to the data.

analyzing the data support $a=\frac{1}{3}$: (i) The best fit of $R_2(t)$ to the three-parameter form $R(t)=B+At^a$ in the time range $1000<t<20000$ gives $a=0.337\pm0.008$. (ii) From an analysis of the $\ln R_2(t)$ versus $\ln t$ plot we find that the slope monotonically increases (apart from some small fluctuations) starting from 0.24 at early time to 0.31 at late times. Also the effective exponent calculated as $\ln[R_2(10t)/R_2(t)]/\ln(10)$ extrapolates to 0.335 ± 0.010 when plotted against $1/R_2(t)$. We found that $R_1(t)$ shows the same qualitative behavior although the errors in $R_1(t)$ make it difficult to get as accurate a determination of the growth law exponent.

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 U.S.-Spain Grant No. CCB-8402/025.

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