Test of the Validity of the Classical Theory of Spinodal Decomposition

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Spinodal decomposition has been studied for a binary system with medium-range interactions. The results indicate that the classical theory of Cahn and Hilliard, which predicts an exponential growth of the structure factor for small wave vectors, holds for a certain range of composition within the spinodal region for short times after a quench.

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Spinodal decomposition refers to a phase separation in an initially unstable system. An alloy or binary mixture is quenched from the one-phase region into the miscibility gap and undergoes phase separation into, say A-rich and B-rich domains. In the classical theory of Cahn and Hilliard[1,2] this process takes place by long-wavelength fluctuations, i.e., the structure factor increases exponentially for wave vectors k smaller than a critical k_c. Such a behavior has not been observed in experiments[3,4] and also not in Monte Carlo simulations[5,6] of binary systems with nearest-neighbor interaction. However, recently experiments on polymer blends[7] showed an exponential increase in the scattering intensity.

In this paper we investigate the process of phase separation in a model binary system with medium-range interaction. Such a system has nearly mean-field-like behavior[8,9] and can be mapped onto the polymer problem[10] where the chain length plays the role of the interaction range.

The Cahn-Hilliard theory of spinodal decomposition rests on the assumption that a coarse-grained free energy

$$F(c)=\int_V [\tfrac{1}{2}\kappa(\nabla c)^2+f(c)]\,dr \tag{1}$$

can be defined in the two-phase region with a coarse-grained free energy density $f(c)$. The coefficient κ is taken to be $\kappa=k_B T_c R^2$, where R is the interaction range. Since we will be concerned with medium-range interactions[8,9,11] we subsequently assume that $f(c)$ is given by its mean-field approximation

$$f(c)=k_B T[c\ln c+(1-c)\ln(1-c)+2c(1-c)T_c/T]. \tag{2}$$

To derive a prediction for the evolution of the structure factor, which is proportional to the small-angle diffuse scattering intensity,[12] after a fast quench into the miscibility gap, one starts from the diffusion equation

$$\partial c(r)/\partial t=M\nabla^2\delta F/\delta c+\xi(r,t)=M\nabla^2(-\kappa\nabla^2 c+\partial f/\partial c)+\xi(r,t), \tag{3}$$

with a random noise term $\xi(r,t)$ included by Cook[13] to ensure the correct statistical description of the system dynamics. M is a mobility. Linearization of Eq. (3) leads to the prediction[11] for the structure factor $S(k,t)$

$$S(k,t)=S(k,0)\exp[\omega(k)t]+S_T(k)\{1-\exp[\omega(k)t]\}, \tag{4}$$

with $S_T(k)$ being the Ornstein-Zernike[14] equilibrium structure factor. The amplification factor $\omega(k)$ in this theory is given by

$$\omega(k)=-2MK^2(\kappa k^2+\partial^2 f/\partial c^2|_{c_0}). \tag{5}$$

For $\partial^2 f/\partial c^2<0$ (inside the spinodal region) there exists a critical wave vector

$$\kappa_c=[(1/\kappa)|\partial^2 f/\partial c^2|]^{1/2}, \tag{6}$$

such that the amplification factor is positive for $k<k_c$. Hence the Cahn-Hilliard theory predicts that long-wavelength fluctuations will grow exponentially and that the maximum growth occurs at $k_m=k_c/\sqrt{2}$, i.e., the peak of the structure factor remains stationary.

The validity of the linearized Cahn-Hilliard theory has been discussed by Binder.[10] He obtained a Ginzburg criterion which gives a range of concentrations where the theory holds for short times after the quench:

$$1 \ll R^3(1-T/T_c)^{1/2}(1-c/c_{sp})^{3/2}. \tag{7}$$

The subscript refers to the spinodal concentration $(\partial^2 f/\partial c^2=0)$.

The process of spinodal decomposition is studied by Monte Carlo simulations of a model A-B sys-

tem. With each lattice site of a simple cubic lattice of $N=L^3$ sites ($L=60$, with periodic boundary conditions) is associated an occupation variable $\eta(r_i)$ which takes on the values $+1$ (occupation with an A atom) or -1 (B atom). The relative concentration of A atoms is $c=(1+\bar{\eta})/2$, where $\bar{\eta}=N^{-1}\sum_i \eta(r_i)$. In this model each lattice site interacts with q neighbors ($q=124$) with equal interaction strength $J/k_BT=\frac{4}{9}(1/q)$.[15] This yields an interaction range of $R=1.42$. To wash out the fluctuations sufficiently, especially for the small wave vectors, five runs were made for the wave vectors $k=(2\pi/L)n$ with $n=5,\ldots,9$ and 19 runs for $n=1,\ldots,4$, which took roughly 190 h computer time.

Initially the A and B atoms were distributed randomly, corresponding to an infinite temperature with a uniform composition. The system was then quenched to the temperature $T/T_c=\frac{4}{9}$ and evolved via exchanges of nearest-neighbor atoms.[16]

The structure factor was computed from the Fourier transform of the pair-correlation function and spherically averaged[5,6]:

$$S(k,t)=\sum{}'S(\vec{k},t)/\sum{}'1, \quad k=(2\pi/L)n, \qquad (8)$$

where $n=1,\ldots,9$. $\sum'$ denotes that for a given n a spherical shell is taken as $n-\frac{1}{2}\leq|\vec{k}|L/2\pi\leq n+\frac{1}{2}$.

For the Ginzburg criterion (7) we expect the linearized Cahn-Hilliard theory to hold for short times after the quench for concentrations $0.35<c<0.65$. The evolution of the structure factor is shown in Fig. 1 for the first five wave vectors. Initially the structure factor indeed increases exponentially and then changes to nonexponential behavior. For the small k vectors the time where exponential growth was observed was roughly five Monte Carlo steps per atom (MCA) ($c=0.4$) and decreased to three MCA for the larger k vectors. For the other two concentrations ($c=0.35, 0.24$) the time decreased to two MCA for the small k vectors to less than one MCA for the larger k vectors. For comparison we have plotted the data of Marro[17] for the short-range model ($q=6, L=30$) in Fig. 2. It is evident that the structure factor does not in-

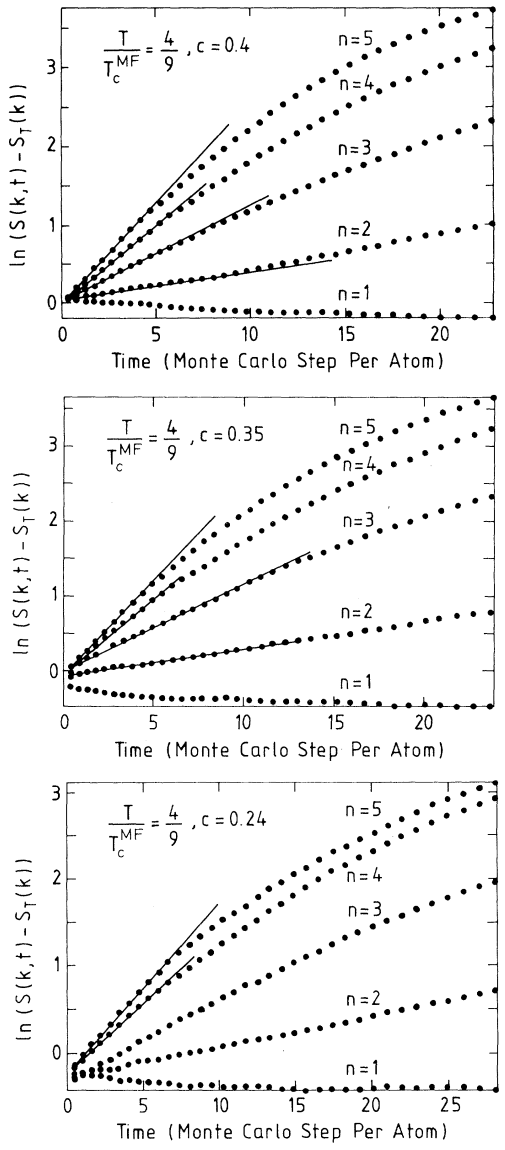

FIG. 1. Evolution of the structure factor after the quench into the miscibility gap of a binary system with concentrations $c=0.4$, 0.35, and 0.24 plotted semilogarithmically. The Cahn-Hilliard theory predicts an exponential growth.

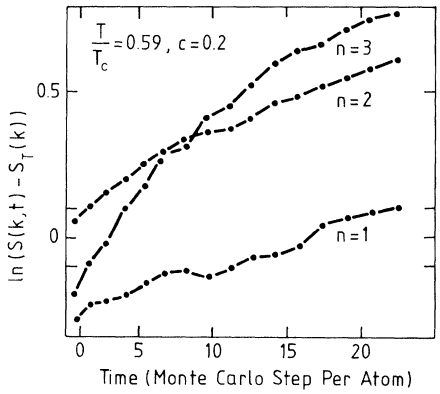

FIG. 2. Semilogarithmic plot of the structure factor after the quench for the short-range model ($q=6, L=30$). The data were taken from Marro (Ref. 17).

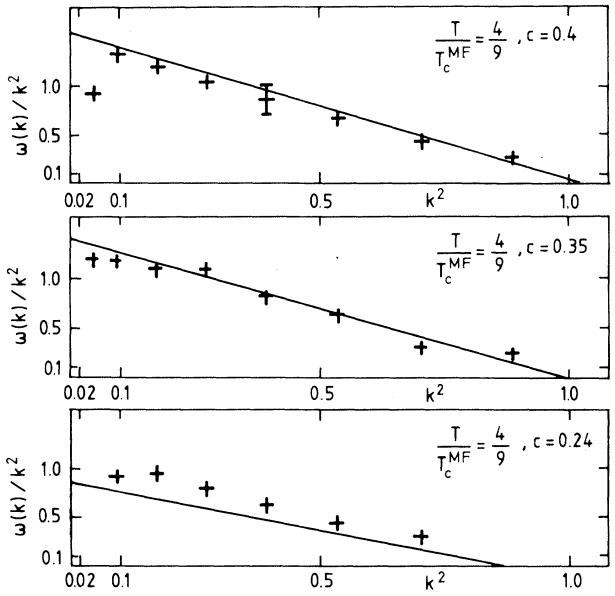

FIG. 3. Amplification factor $\omega(k)$ of the structure factor divided by the square of the wave vector plotted vs the square of the wave vector. The straight lines are the mean-field predictions.

crease exponentially in the nearest-neighbor model. Figure 3 shows the results for the amplification factor $\omega(k)$ divided by k^2 versus k^2 for concentrations $c=0.4$, 0.35, and 0.24, which should give a straight line. The data points were obtained from the logarithmic time derivative of the structure factor, taking into account the equilibrium structure factor $S_T(k)$. For the concentration $c=0.4$ the data follow the prediction of the Cahn-Hilliard theory. The deviation of the second wave vector is due to finite-size effects and the limited statistics. A reduction of the error bars is, however, only possible with substantially more computer time. The agreement gets worse for the other two concentrations, as expected from (7).

To summarize, the Monte Carlo simulations of a medium-range model indicate that Cahn's linearized theory of spinodal decomposition holds to a very good approximation for a short time after the quench for a certain range of compositions given by a Ginzburg criterion.[18] It becomes exact, however, only in the limit of infinite interaction range. In this limit one can come arbitrarily close to the spinodal singularity.[9] For medium-range interaction the linear theory becomes worse as one approaches the spinodal and ultimately breaks down. It remains a challenge for future theories to go in a systematic way beyond the linear approximation and describe the transition region between classical nucleation theory and classical spinodal decomposition. The present results anyway explain why in systems such as polymer mixtures the concept of the linear theory is much better defined than for short-range systems.

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