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Volume-fraction dependence of scaling functions in phase-separation processes of binary mixtures

Amitabha Chakrabarti
Department of Physics, Kansas State University, Manhattan, Kansas 66506

Raúl Toral
Departament de Física, Universitat de les Illes Balears, E-07071 Palma de Mallorca, Spain

James D. Gunton
Department of Physics, Lehigh University, Bethlehem, Pennsylvania 18015
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We present results of a numerical study of the Cahn-Hilliard model of phase separation for a binary mixture quenched deep in the nucleation regime. We study the volume-fraction dependence of the scaling functions for the pair correlation function and the structure factor. Our results indicate that for small volume fraction ϕ the shape of the scaling functions depends strongly on ϕ, whereas for larger volume fractions the scaling functions seem to be independent of ϕ.

An important question in the study of phase-separation processes[1] is the effect of varying the volume fraction (ϕ) of the minority constituent of the binary mixture on experimentally measured quantities such as the scattering intensity of radiations. In particular, one is interested in the dependence of the time-independent scaling function (obtained from the scattering intensity after suitably rescaling the wave vectors by a time-dependent characteristic length scale) on the volume fraction. Several analytical studies[2–6] have been carried out to obtain the volume fraction dependence of the scaling functions for the structure factor. Among these calculations, the theory of Tokuyama, Enomoto, and Kawasaki[2] seems to be the most complete one, since it considers both initial thermal fluctuations and nonthermal fluctuations generated by soft collision among droplets. This theory predicts a strong dependence of the shape of the scaling functions on the volume fraction ϕ. The theory is, however, applicable only in the limit of small volume fraction ϕ (typically $\phi < 10\%$) and unfortunately cannot be extended for the case of larger volume fractions due to the perturbative nature of the calculations. Numerical studies, on the other hand, have recently been carried out in two dimensions for larger volume fractions and could not detect[7] any appreciable dependence of the scaling function on ϕ even when the volume fraction is changed from 50% to about 21%. Since the analytical studies break down for large volume fractions and the numerical studies are difficult to carry out for small volume fractions due to finite size limitations, it has been possible to compare even the qualitative features of the scaling functions seen in the analytical studies with the numerical simulations.

In this paper we report results from a numerical study of a model of phase separation (the Cahn-Hilliard[8] model) for volume fraction as small as 5% for one of the constituents. Although the numerical study is carried out in two dimensions (due to computer-time limitations) and the analytical study of Tokuyama, Enomoto, and Kawasaki[2] is valid only in three dimensions, the small volume fraction used in the present study allows us to compare the qualitative features of the scaling function calculated in the simulations and the theory. Our main results are as follows: Although no appreciable change in the shape of the scaling functions was found before[7] for volume fractions $\phi=50\%$ and $\phi=21\%$, we find that the scaling functions for $\phi=5\%$ and $\phi=21\%$ are distinctly different both for the structure factor and the pair correlation functions. This is a striking result in the sense that both for $\phi=5\%$ and $\phi=21\%$ the morphology of the system is similar to each other and is comprised of droplets, whereas for $\phi=50\%$ the morphology is interconnected and is radically different from that with either $\phi=5\%$ or $\phi=21\%$.

The standard Cahn-Hilliard equation of motion for the concentration field $\psi(\mathbf{r},t)$ is

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

where M is the constant mobility, b, u and K are phenomenological positive constants, and thermal noise is neglected in this model. Equation (1) can be written in a simpler form after rescaling $\psi(\mathbf{r},t)$ by $(b/u)^{1/2}$, the dis-

tance by $(K/b)^{1/2}$, and the time by $2K/Mb^2$. The resulting parameterless equation

$$\frac{\partial\psi(\mathbf{r},t)}{\partial t}=\frac{1}{2}\nabla^2[-\psi+\psi^3-\nabla^2\psi]\ , \tag{2}$$

has been the subject of several recent numerical studies in both two[7,9–12] and three[13] dimensions.

A numerical study of Eq. (2) is very demanding on computer resources (both from the point of central processing unit time and memory requirements) particularly for small volume fractions due to the following reason: For small volume fractions, one would need to consider a very large system size such that the minority phase has enough matter in it to produce several droplets of different size, so that a statistical analysis of the dynamics is meaningful. The finite-size effect becomes more prominent at late times since the number of droplets decreases with time. On the other hand, the evolution of the system needs to be studied out to late enough times so that the system is in the so-called scaling regime. Thus one needs to consider a very large lattice size in the simulation, such that at late enough times in the scaling regime, one still has a large number of droplets of the minority phase. We have numerically integrated Eq. (2) on a square lattice of size 540^2 using a second-order Runge-Kutta scheme and with periodic boundary conditions. The specific details of the numerical integration will be given elsewhere.[14] For small volume fractions, one needs to be careful with the initial conditions as well. Since the system is in the metastable region of the phase diagram in this case, a strong fluctuation is needed in the initial distribution of the order parameter in order to allow for growth of the initial random nuclei. We chose the initial configuration of $\psi(\mathbf{r},t)$ to be Gaussian distributed with center at $\psi_0=0.9$ and with a variance of magnitude 5. A final adjustment is made in order to have the mean value of the field $\langle\psi\rangle$ exactly equal to ψ_0. For this particular choice of the initial configuration the magnitude of the order parameter can be very large at random points on the lattice, so that initially one needs a very small time step for the stability of the numerical integration. However, the order parameter settles down to values smaller than unity very soon and then the time step can be increased safely. We have carried out the numerical integration up to $t=20000$ in the above-mentioned units. The mesh size is fixed at $\delta x=1.0$ and the time step chosen is as follows: From $t=0$ to $t=100$ the time step is chosen to be $\delta t=0.001$, from $t=100$ to $t=1000$ the time step is chosen to be $\delta t=0.025$ and for $t>1000$, δt is fixed at 0.05. In order to average over the initial random configurations, we have performed 60 runs with different initial configurations.

It is well established by now that the late stages of the phase separation process can be described in terms of scaling with a time dependent length.[1,15–17] The fundamental assumption of scaling is that, in the late stages of the evolution process, only one length, $R(t)$, is relevant. This characteristic length represents a measure of the typical domain size and increases with time. A main feature emerging from this picture 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

$$G(\mathbf{r},t)=g(\mathbf{r}/R(t)) \tag{3}$$

and

$$S(\mathbf{k},t)=R(t)^dF(\mathbf{k}R(t))\ , \tag{4}$$

where d is the dimensionality of the system. The functions $g(x)$ and $F(x)$ are the time independent scaling functions of the system.

The scaling function defined in Eq. (3) is shown in Fig. 1 for the circularly averaged and normalized correlation function $G_n(r,t)$ for different volume fractions ϕ of one of the constituents of the binary mixture. Here $G_n(r,t)$ is defined to be $G(r,t)/G(0,t)$, i.e.,

$$G_n(r,t)=\frac{G(r,t)}{\langle\psi^2(t)\rangle-\langle\psi\rangle^2} \tag{5}$$

such that $G_n(0,t)$ is equal to unity for all t. In Fig. 1, $R(t)$ is defined as the coordinate of the first zero of $G_n(r,t)$ which is denoted as $R_g(t)$. It is clear that the scaling function of $\phi=5\%$ is distinctly different from that of either $\phi=21\%$ or $\phi=50\%$ (the last two are, on the other hand, very similar to each other). The interesting feature of the scaling function for $\phi=5\%$ is that the oscillations seen in the scaling function for larger volume fractions are almost absent here and the magnitude of the pair correlation function is very small for $r>R_g$. This suggests that the spatial correlations among the droplets are much weaker in this case.

Figure 2 shows the data for the circularly averaged and normalized structure factor $S(k,t)$ plotted to verify the scaling ansatz Eq. (4) for $\phi=5\%$. In this plot we have used the average radius of gyration $R_G(t)$ of the droplets as a typical measure for the domain size $R(t)$. As can be seen in this figure, scaling holds quite well for $t>10\,000$. In Fig. 3 we compare the scaling functions for $\phi=21\%$

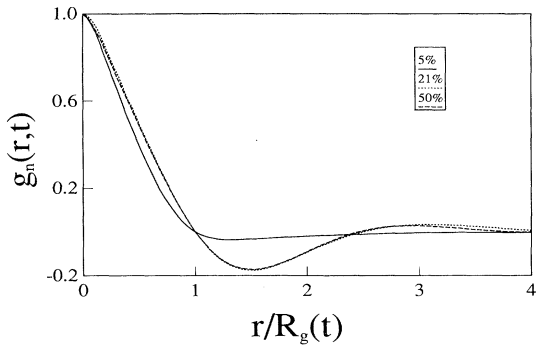

FIG. 1. Scaling function corresponding to the circularly averaged and normalized pair correlation function $G_n(r,t)$ [Eq. (3)] vs r/R_g for different volume fractions ϕ. Here R_g is the location of the first zero of $G_n(r,t)$. Note that the scaling function is very similar for $\phi=50\%$ and $\phi=21\%$ whereas it differs significantly from the above ones for $\phi=5\%$. The scaling functions for $\phi=50\%$ and $\phi=21\%$ are taken from Refs. 11 and 7, respectively.

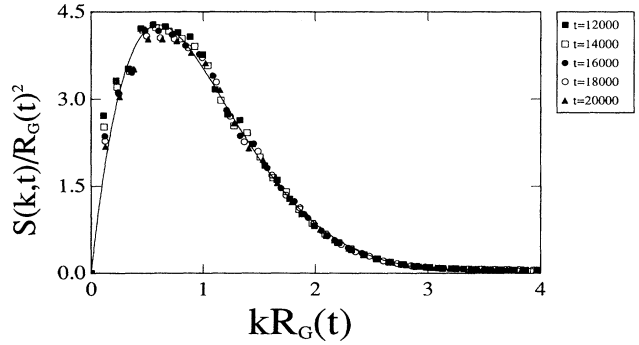

FIG. 2. Data for the circularly averaged and normalized [by $G(0,t)$] structure factor $S(k,t)$ plotted to verify the scaling ansatz Eq. (4) for $\phi=5\%$. In this plot we have used the average radius of gyration $R_G(t)$ of the droplets as a typical measure for the domain size $R(t)$. As can be seen in this figure, scaling holds quite well for $t>10\,000$. The solid line is a guide to the eye.

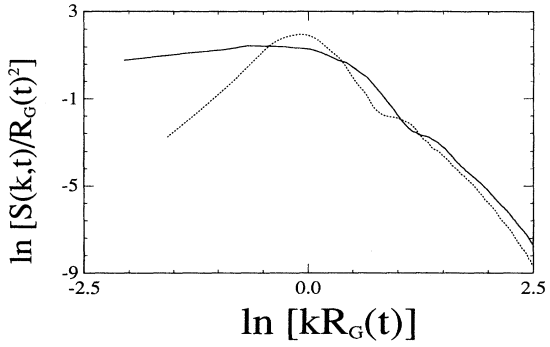

FIG. 4. Scaling functions of Fig. 3 plotted in a log-log plot. Note the presence of a secondary maxima or shoulder in both scaling functions for large k values. Note also that although the two scaling functions are more or less parallel to each other for large k values, their functional forms are very much different for small values of k.

and $\phi=5\%$. Since the scaling functions for $\phi=21\%$ and $\phi=50\%$ agree well with each other the scaling function for 50% is not included in this figure. Again we see that the scaling functions are quite different for these two volume fractions.

Let us now compare the qualitative features of the scaling functions computed here with those found in the theoretical calculations of Tokuyama, Enomoto, and Kawasaki[2] for three-dimensional systems. Comparing the scaling functions in Fig. 3 we find that as the volume fraction is decreased, the half-width of the scaling functions increase, the location of the peak of the scaling function shifts toward smaller reduced wave vectors and the peak height decreases. *All* of these features are in good qualitative agreement with the above theory.

In Fig. 4 we show the same data of Fig. 3 in a log-log plot. It is easy to determine the small and large (reduced) wave-vector behavior of the scaling function if plotted in this fashion. Several important features are evident from this figure. First of all, a secondary maxima shows up in both of the scaling functions for large k values. However, the locations of the secondary maxima is slightly different for the two volume fractions considered in the figure. This type of secondary maxima or shoulders have been observed in experiments with polymer mixtures[18] as well as in theoretical[3,19] and numerical[20] calculations. Another important feature is that although the two scaling functions are more or less parallel to each other for large k values, their functional forms are very much different for small values of k. For small k the scaling function increases approximately as k^4 for $\phi=21\%$ in accordance with recent theories,[21,22] whereas for $\phi=5\%$ the scaling function seems to be quite flat for small wave vectors.

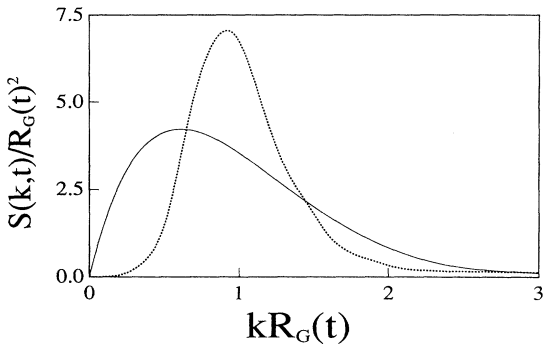

FIG. 3. Comparison of the scaling function for the structure for $\phi=21\%$ (dotted line) and $\phi=5\%$ (solid line). Since the scaling functions for $\phi=21\%$ and $\phi=50\%$ agree well with each other (see Ref. 7), the scaling function for $\phi=50\%$ is not included in this figure. The scaling functions are quite different for these two volume fractions and the qualitative features of the scaling functions agree well with Ref. 2 (see text).

In summary, we conclude that we have carried out a numerical study of the Cahn-Hilliard model for a quench deep in the nucleation regime of the phase diagram. We have studied the volume fraction dependence of the scaling functions for the pair correlation function and the structure factor in two dimensions. Our results indicate that for a small volume fraction ϕ the shape of the scaling functions depend strongly on ϕ whereas for larger volume fractions, the scaling functions seem to be independent of ϕ, at least within the numerical accuracy. In the absence of any good theory in two dimensions, the qualitative features of the results are compared with analytical theories valid in three dimensions[23] and for small volume fractions.[2] Comparison with our results for the scaling functions for different volume fractions will be a good test for any future theory in two dimensions.

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