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Scaling behavior of a model of block copolymers in three dimensions

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We have studied the dynamical and equilibrium scaling behaviors of a coarse-grained model for microphase separation of block copolymers. Our numerical study has been carried out in three dimensions. We compute the power-law exponent θ characterizing the equilibrium microdomain size R_{eq} as a function of the molecular weight of the copolymers N as $R_{\text{eq}} \sim N^{\theta}$, and conclude that we are able to study the weak-segregation regime, but not the true strong-segregation regime of the model. We have also tested scaling hypotheses connecting the microdomain size and the equilibrium structure factor of the block copolymers.

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I. INTRODUCTION

When a binary mixture of atomic or small molecular systems (such as a metal alloy) is rapidly quenched from an initial high-temperature uniform phase to a point deep inside the coexistence curve, *macroscopic domains* rich in one or the other component of the mixture are formed [1]. For late stages of this phase-separation process, the characteristic size of the domains, $R(t)$, grows as a power law with time [2–4] as $R(t) \sim t^{1/3}$. Moreover, the late stages of the phase-separation process can be described in terms of scaling [1,5,6] with the same time-dependent length $R(t)$. A main feature emerging from this scaling 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

$$G(\mathbf{r},t)=g(\mathbf{r}/R(t)) \tag{1}$$

and

$$S(\mathbf{k},t)=R(t)^{d}\cdot s(\mathbf{k}\cdot R(t)) , \tag{2}$$

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

The situation is quite different in a block copolymer [7] (BCP) melt, in which the phase-separation process proceeds in a different fashion due to the molecular structure of the copolymers. A diblock copolymer melt is composed of long chain molecules consisting of two covalently bonded subchains of constituent monomers of A type and B type, respectively. When the two species are mutually incompatible, a phase separation can occur at low enough temperatures. However, due to the covalent bond between the A and B chains, phase separation cannot proceed to a macroscopic scale; instead *microdomains* rich in either of the two components are formed [8]. The distinctive properties of these structures have been attracting a lot of interest recently [9–26] due, in part, to the great technological importance of the block copolymer materials. In experiments one finds that the system can form periodic lamellar, spherical, or cylindrical structures depending on the relative chain length of the two cobonded polymers and on the amount of solvent present in the mixture [9–12]. It also has been found experimentally [11–14] that the equilibrium mean thickness D of these microdomains scales as the molecular weight N of the copolymers as $D \sim N^{\theta}$. One usually distinguishes between two scaling regimes [15–19] to characterize the value of the exponent θ: a strong-segregation regime and a weak-segregation regime. If the A-B segment-segment (Flory) interaction parameter χ is such that χN is less than a critical value (typically of the order of 10), the copolymer is in a disordered state, whereas for larger values of χN an order-to-disorder transition takes place. A system in the ordered state but close to the order-disorder transition point is said to be in the weak-segregation limit and experiments in this limit yield $\theta=\frac{1}{2}$. On the other hand, for $\chi N \gg 10$ the system is in the strong-segregation regime and $\theta=\frac{2}{3}$ has been observed in experiments. It should be noted here that in some recent experiments [13,14] a larger value of θ ($\theta \approx 0.8$) was found. This was argued [14] to describe a crossover behavior from the weak-segregation to the strong-segregation regime.

Theoretical studies of phase separation in block copolymers have been carried out by several authors. Helfand and Wasserman [15] use an analogy between the conformation of a polymer chain and the trajectory of a Brownian particle to write down the free energy for the ordered state of a block-copolymer system under strong segregation. When this free energy is minimized with respect to D, they find that $\theta=0.636$, which compares well to the value of θ found in some experiments. A different approach has been taken by Leibler [16] based on a local order-parameter formulation. His analysis is restricted to the weak-segregation limit and predicts $D \sim N^{1/2}$, in agreement with experimental results in that limit. Ohta and Kawasaki [17] use a method similar to Leibler but incorporate long-range interactions, arising from the connectivity of different monomer sequences in a copolymer chain, and recover $\theta=\frac{2}{3}$ for the strong-segregation limit. Also, the crossover behavior of D between the weak-segregation and strong-segregation limits can be described [18,16] by $D \sim N^{1/2} f(\chi N)$, where the crossover scaling function $f(x)$ is given by $f(x) \to 1$ for $x \to 0$ and $f(x) \to x^{1/6}$ for $x \to \infty$.

Recently, Oono and his group [20–22] proposed phenomenological models for the phase-separation dynamics for the block-copolymer system. They start from a coarse-grained description of the ordering process in a similar fashion to the Cahn-Hilliard (CH) model [1,27] used to study phase separation in binary alloys. In the CH formulation, one writes the time variation of the concentration field $\phi(\mathbf{r},t)$ in terms of a variational derivative of a local free-energy functional given by the Ginzburg-Landau expression. The resulting equation of motion can then be written as

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

where M is the constant mobility, b, u, and K are phenomenological positive constants, and the thermal noise is neglected in this model. At low temperatures, the noise term is not thought to affect some important features of the late stages of the evolution [28], such as the growth law for the characteristic domain size and the scaling functions. The fact that the equilibrium configurations in a block-copolymer system are made out of microdomains is incorporated by Oono and his colleagues by modifying the previous equation for the coarse-grained order-parameter field $\phi(\mathbf{r},t)$ in the following way:

$$\frac{\partial \phi(\mathbf{r},t)}{\partial t} = M\nabla^2(-b\phi + u\phi^3 - K\nabla^2\phi) - B\phi, \tag{4}$$

where B is another phenomenological parameter. This equation is the same as the CH equation [Eq. (3)] except for the presence of the $-B\phi$ term. This last term, $-B\phi$, makes the $\phi=0$ state more stable than that with $\phi \neq 0$ in the absence of spatial gradients. Thus, the domain size saturates at an equilibrium value after an initial increment with time. Oono and Bahiana [21,22] studied a cell-dynamics [29] version of Eq. (4) in two dimensions in the weak-segregation limit. They conclude empirically that B is proportional to N^{-2} and on the basis of that find $\theta=\frac{1}{2}$.

In this paper we have carried out a detailed study of the model proposed by Oono and his group [Eq. (4)] in three dimensions by using a numerical integration approach. We compute θ and study dynamical and equilibrium scaling hypotheses proposed in recent works [23,24]. The paper is organized as follows. In Sec. II we describe the model and the numerical procedures used in the study, in Sec. III we present our main results, and in Sec. IV we conclude with a brief summary and discussions.

II. MODEL AND NUMERICAL PROCEDURE

Equation (4) can be written in a simpler form after rescaling $\phi(\mathbf{r},t)$ by $(b/u)^{1/2}$, the distance by $(K/b)^{1/2}$, and the time by $2K/Mb^2$. The resulting parameterless equation reads

$$\frac{\partial \phi(\mathbf{r},t)}{\partial t} = \tfrac{1}{2}\nabla^2(-\phi + \phi^3 - \nabla^2\phi) - \epsilon\phi, \tag{5}$$

where ϵ is the only parameter of the model. We consider a critical quench with the order parameter equal to zero. This situation corresponds to the case where the A and B blocks of the diblock copolymers are of the same length. One can show that the order parameter is conserved in the above model for a critical quench in the following way. If we denote

$$\psi(t) = \int \phi(\mathbf{r},t)\,d\mathbf{r} \tag{6}$$

to be the order parameter, then by integrating Eq. (5) over all space one finds

$$\frac{\partial \psi(t)}{\partial t} = -\epsilon\psi(t) \tag{7}$$

since the Laplacian term vanishes after integration. The solution of the above equation is

$$\psi(t) = \psi(0)e^{-\epsilon t}. \tag{8}$$

For a critical quench, the order parameter is zero, i.e., $\psi(0)=0$ and thus $\psi(t)$ is zero at all times, conserving the order parameter.

A numerical study of Eq. (5) in three dimensions is very demanding on computer resources (from the standpoint of both central processing unit time and memory requirements) due to the fact that one needs to run the system to equilibrium. Also, one needs to consider different values of the parameter ϵ for the scaling analysis and for each ϵ the results need to be averaged over several initial configurations of the concentration field. In these calculations we have used a finite difference scheme for both the spatial and temporal derivatives. The spatial discretization is achieved by replacing the continuous space of position vectors $\mathbf{r}=(x,y,z)$ by a simple cubic lattice with $N=L^3$ sites and lattice spacing δr. Periodic boundary conditions are assumed in order to avoid the surface effects. We integrate numerically Eq. (5) by using a first-order Euler scheme. In order to carry out the calculations within a reasonable amount of computer time, one should choose a large time step and a moderately large system size. However, the discretized version of Eq. (5) would develop a subharmonic "bifurcation instability" for large time steps [28]. Following our previous works [2] on the Cahn-Hilliard model in three dimensions, we have chosen the mesh size $\delta r=1.7$ and the time step $\Delta t=0.1$. We have found that smaller values of Δt do not change quantities that express a global behavior, such as the structure function, the pair-correlation function, or the typical (micro)domain size. We have considered a simple cubic lattice with $L=50$, which is equivalent to saying that the linear dimension of the system (in the dimensionless units described before) $L_a=85$ units. We have considered ten different values for the parameter ϵ between 0.01 and 0.1. We chose the initial field configurations to be uniformly distributed between -0.1 and 0.1 with the order parameter strictly equal to zero. In order to average over the initial random configurations, we have performed ten runs for each value of ϵ.

III. RESULTS

In Figs. 1–3 we show typical cross sections of the system at equilibrium for three different values of ϵ. In Fig. 1, where $\epsilon=0.01$, the cross section shows the typical characteristic of the interconnected pattern of a spinodally decomposing system. A similar pattern for a block-copolymer system has been observed in previous two-dimensional simulations [20,21] of this model. However, when ϵ is increased, we find that the equilibrium pattern shows more and more ordered structures and the presence of a lamellar structure seems to be developing. This kind of ordered structure has been observed in experiments in cross sections of thick films of block copolymers [9,10].

For the equilibrium pattern in the above model, a scaling description has been suggested by Oono and his group. Using a dimensional analysis and comparing the equilibrium properties of the model with the CH equation (i.e., $\epsilon=0$), they argue that $[\epsilon^{-1}]$ corresponds to $[t]$ and also $[\epsilon^{-1}]$ corresponds to $[l^4]$, where l is a characteristic length of the system that is identified as $N^{1/2}$. Thus, $[N^2]$ corresponds to $[t]$ and the asymptotic growth law $l(t)\sim t^n$ for the CH equation corresponds to $l\sim N^{2n}$ for block copolymers, i.e., $\theta=2n$. For spinodal decomposition the accepted [2–4] asymptotic growth law exponent is $n=\frac{1}{3}$, which implies $\theta=\frac{2}{3}$, and this agrees very well with the experimental results in the strong-segregation limit. However, it is extremely difficult to reach the strong-segregation limit in numerical simulations and one finds $\theta=\frac{1}{2}$. This is the weak-segregation limit. It corresponds to the *early* stages of spinodal decomposition, in which the interface thickness is appreciable and surface diffusion dominates. In this case [1,30] $l\sim t^{1/4}$, which corresponds to $\theta=\frac{1}{2}$ for block copolymers.

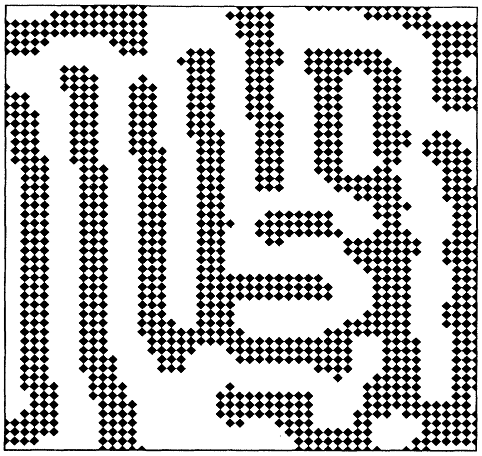

FIG. 2. A typical cross section of the system for $\epsilon=0.05$.

In order to find the exponent θ from our simulation, we calculate the microdomain size in the equilibrium as in earlier studies: We calculate the pair-correlation function $g(r,t,\epsilon)$ and define the location of the first zero of this pair-correlation function, $R(t,\epsilon)$, as a measure of the microdomain size. When the system reaches equilibrium, $R(t,\epsilon)$ becomes independent of t and we take the value $R_{\text{eq}}(\epsilon)$ as a measure of the characteristic size of the microdomains in equilibrium (D). In Fig. 4 we show a log-log plot of $R_{\text{eq}}(\epsilon)$ vs ϵ. We find that the best fit to the

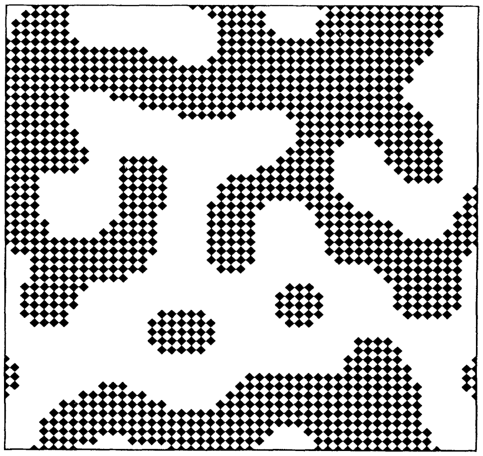

FIG. 1. A typical cross section of the system for $\epsilon=0.01$.

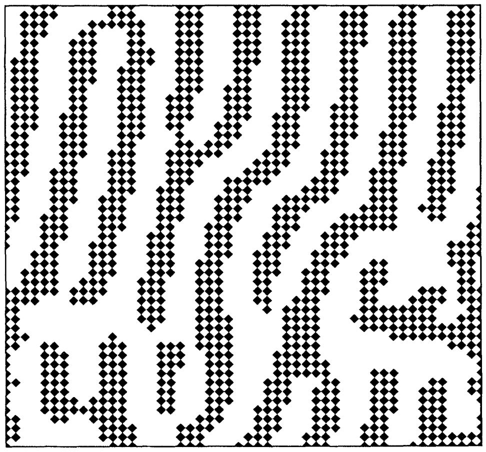

FIG. 3. A typical cross section of the system for $\epsilon=0.1$. Comparing with Figs. 1 and 2 we note that the ordered lamellar structures become more and more evident as ϵ increases.

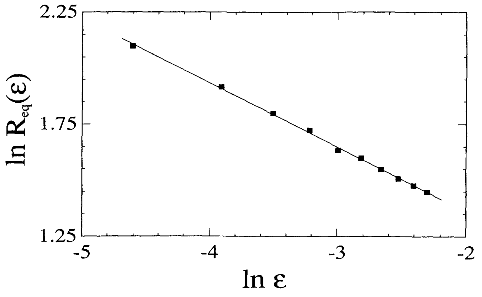

FIG. 4. Log-log plot of $R_{\rm eq}(\epsilon)$ vs ϵ. The straight line is the best fit to the data yielding an exponent -0.29 ± 0.01. The exponent θ (see text) is thus $\theta\approx0.58$.

data yields an exponent of -0.29 ± 0.01, which, using the above identification $\epsilon\sim N^{-2}$, corresponds to $\theta\approx0.58$. This number is larger than that for the weak-segregation limit but smaller than that for the strong-segregation limit. This indicates that our simulation study did not probe the true strong-segregation regime of the model. In order to see the strong-segregation regime, the molecular weight N of the block copolymers needs to be much larger. Since the parameter $\epsilon\sim N^{-2}$, this means that the parameter ϵ needs to be much smaller than considered in this study. However, for smaller values of ϵ it is extremely difficult in numerical studies to reach equilibrium. (For the system size considered here, the equilibration time is already close to $t=10\,000$ when $\epsilon=0.01$.) Also, since the equilibrium domain size is going to be much larger when ϵ is smaller, one needs to consider larger lattice size as well in order to avoid finite-size effects. Thus, the strong-segregation regime for a numerical study of this model seems to be beyond reach at this point.

A scaling hypothesis for the characteristic length $R(t,\epsilon)$ has been proposed by Liu and Goldenfeld [23]. They propose a scaling form

$$R(t,\epsilon)=\epsilon^{-\theta/2}F(t\epsilon)\ , \tag{9}$$

where $F(x)$ is a scaling function independent of t and ϵ. We show our data for $R(t,\epsilon)$ vs $\ln t$ for various values of ϵ in Fig. 5 and test the above scaling form [Eq. (9)] in Fig. 6 by taking $\theta=0.58$, which was obtained earlier. As can be seen from Fig. 6, the scaling works fairly well.

The suggestion of Oono and colleagues that there is a correspondence between the block-copolymer system and spinodally decomposing system (with N^2 corresponding to t in the two cases) is studied in Fig. 7. In this figure we plot the equilibrium structure factor $S(k,\epsilon)$ for the block-copolymer system against k for different values of ϵ. As ϵ is decreased, the structure factor becomes sharper and the location of the peak shifts to smaller values of k. Thus the equilibrium structure factor for block-copolymer systems with decreasing ϵ behaves qualitatively similarly to the time-dependent structure factor $S(k,t)$ for a spinodally decomposing system as t increases after the quench [1].

In order to study the correspondence between the structure factors of the two systems mentioned above, we use a scaling hypothesis [24] for the structure factor of the block-copolymer system as

$$S(k,\epsilon)=R_{\rm eq}(\epsilon)^3F(kR(\epsilon)) \tag{10}$$

in three dimensions. We test this scaling hypothesis in Fig. 8 by plotting $S(k,\epsilon)R_{\rm eq}(\epsilon)^{-3}$ vs $kR(\epsilon)$. In numerical simulations it is not easy to test this scaling hypothesis, due to the fact that the structure factors are very sharply peaked (see Fig. 6) and the lattice discretizations do not leave us with enough data points to accurately determine the structure factors near the peak. This could be responsible for the scatter seen in the data in Fig. 8.

IV. CONCLUSIONS

In summary, then, we have studied a model for microphase separation of block copolymers originally proposed by Oono and colleagues. Our numerical study is carried out in three dimensions by numerically integrating the model equations for a very long time. Even with extensive computations we could not probe the true strong-segregation regime of the model. However, the morphology of our system and the value of the exponent θ characterizing the microdomain size to the molecular weight of

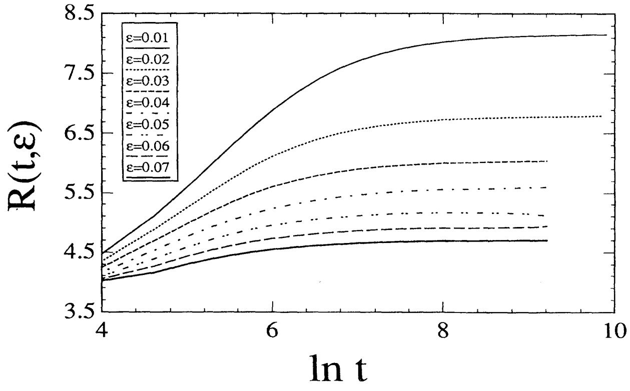

FIG. 5. $R(t,\epsilon)$ vs $\ln t$ for various values of ϵ.

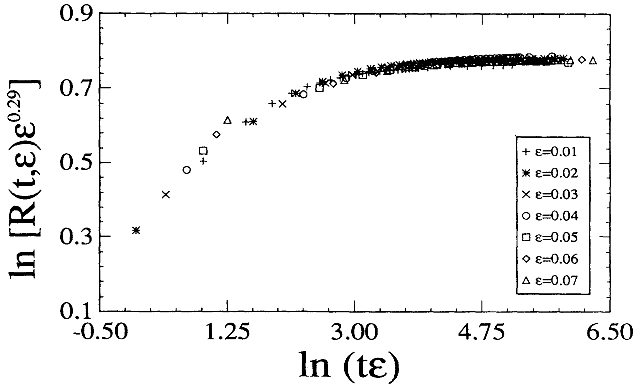

FIG. 6. Test of the scaling hypothesis Eq. (9) for $R(t,\epsilon)$.

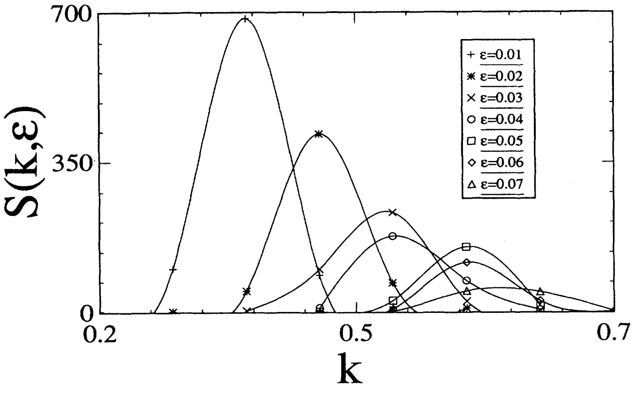

FIG. 7. Plot of the spherically averaged equilibrium structure factor $S(k,\epsilon)$ vs wave vector k for various values of ϵ.

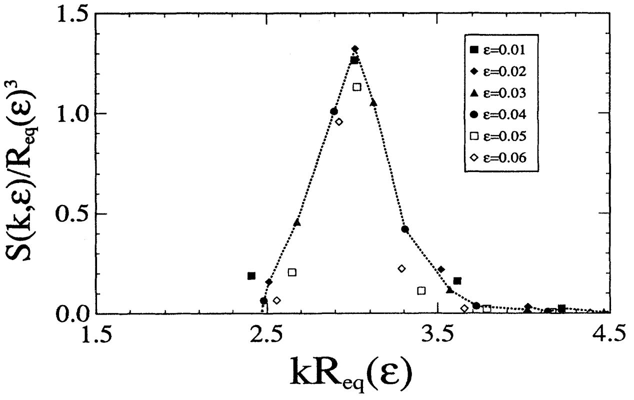

FIG. 8. Test of the scaling hypothesis Eq. (10) for the equilibrium structure factor $S(k,\epsilon)$. The dotted line is a guide to the eye.

the copolymers suggest that we are probably in between the weak-segregation and the strong-segregation regime. We have also found our data to be consistent with a scaling hypothesis for the microdomain size proposed by Liu and Goldenfeld and another scaling hypothesis proposed by us for the equilibrium structure factor.

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