

Microphase Separation in Block Copolymers

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We introduce a microscopic model for the phase separation in block copolymers and carry out Monte Carlo simulations in two dimensions. We find that the equilibrium structure function satisfies a scaling relation with D_{eq} , the thickness of the microdomains. We also find that $D_{\text{eq}} \sim N^\theta$, where N is the chain length and $\theta = \frac{1}{2}$ in the weak-segregation limit, in agreement with calculations in a cell-dynamics model. This suggests that the microscopic and the continuum models of block copolymers are in the same universality class.

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A block-copolymer melt is composed of long chain molecules consisting of two covalently bonded subchains of constituent monomers A and B , respectively.¹ This particular microscopic structure is reflected in several macroscopic properties that make block copolymers of great technological value.² One of the most interesting effects occurs when the two species A and B are mutually incompatible. In that case, a phase separation occurs 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 each of the two components are formed.³ This so-called mesophase formation produces periodic spatial patterns. 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.^{4,5} It has also been found experimentally³ that the thickness, D_{eq} , of these microdomains scales as a power law of the molecular weight N of the copolymers, i.e., $D \sim N^\theta$, where $\theta = \frac{2}{3}$ in the strong-segregation case and $\theta = \frac{1}{2}$ in the weak-segregation case.

In this Letter, we report the results of a numerical simulation of phase separation in block-copolymer systems, using a Monte Carlo-type dynamics for a lattice model consisting of long self-avoiding chains.^{6,7} Our numerical calculations, carried out in the weak-segregation limit, confirm that $\theta = \frac{1}{2}$ in this limit. We also compare our results with those found in a recent coarse-grained model introduced by Oono and co-workers.^{8,9} The comparison strongly suggests that the microscopic kinetic and coarse-grained models belong to the same universality class for block-copolymer melts.

Theoretical studies of phase separation in block copolymers have been carried out by several authors.¹⁰⁻¹² Helfand and Wasserman¹⁰ 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_{eq} , they find that $\theta = 0.636$, which compares

extremely well to the value of θ found in experiments. On the other hand, a different approach based on a local order-parameter formulation has been taken by Leibler.¹¹ His analysis is restricted to the weak-segregation limit and predicts $D_{\text{eq}} \sim N^{1/2}$. Ohta and Kawasaki¹² 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 in a mean-field-type calculation.

Recently, Oono and co-workers^{8,9} have proposed phenomenological models for the phase separation dynamics of the block-copolymer system. They start from a coarse-grained description of the ordering process in a similar fashion to the Cahn-Hilliard-Cook (CHC) model¹³ used to study phase separation in binary alloys. The fact that the equilibrium configurations in a block-copolymer system are made out of microdomains is incorporated by these authors by writing an equation for the coarse-grained order-parameter field $\phi(\mathbf{r}, t)$ in the form

$$\frac{\partial \phi(\mathbf{r}, t)}{\partial t} = M \nabla^2 (-b\phi + u\phi^3 - K \nabla^2 \phi) - B\phi, \quad (1)$$

where b , u , K , M , and B are phenomenological parameters. This equation is the deterministic version of the CHC model except for the presence of the $-B\phi$ term. The 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 Bahiana⁹ studied the cell-dynamics version¹⁴ of Eq. (1) in the weak-segregation limit. They empirically conclude that B is proportional to N^{-2} and on the basis of that find $\theta = \frac{1}{2}$ in the above limit. The partial differential equation describing phase separation in a block-copolymer melt has also been used¹⁵ to numerically construct the periodic solution which minimizes the free energy. All these numerical studies take Eq. (1) as the equation governing the dynamics of phase separation of block-copolymer melts, which is a phenomenological approach

to the real dynamics. Thus, it is particularly worthwhile to study phase separation in block copolymers starting from a *microscopic model*, since such a study can, in principle, test the applicability of these phenomenological models to the study of microdomain formation in block-copolymer systems. In the case of binary alloys, numerical studies of the microscopic kinetic Ising model,^{16,17} the CHC model,¹⁸ and the cell-dynamics model¹⁹ have suggested that these models actually belong to the same universality class²⁰ in the sense that the growth-law exponent of the characteristic domain size and the dynamical scaling functions calculated from the pair correlation function and the structure function are the same, within the numerical accuracy of the studies. However, no such correspondence between the coarse-grained and microscopic models of phase separation in block copolymers exists in the literature.

We model a block-copolymer molecule with N monomer units as a self-avoiding walk of length $N-1$ on a square lattice. The first $N/2$ consecutive monomers are considered as A type and are assigned a spin variable $S_i = +1$. The other monomers are considered to be of B type ($S_i = -1$). We assign an interaction of strength $-J$ when two monomers of the same species (AA or BB) are nearest neighbors, whereas the interactions between A - B pairs are taken as zero. In order to study the molecular-weight dependence of measured quantities, we keep the monomer concentration constant (and equal to 0.6) and, consequently, vary the total number of chains placed on the lattice. The empty lattice sites are treated as solvent molecules and assigned spin variables $S_i = 0$. The lattice under consideration is of size $L^2 = 128^2$; chains with $N = 10, 20, 30,$ and 40 are studied in the simulations. We place the chains randomly in the lattice as self-avoiding random walks (which corresponds to a very-high-temperature configuration) and then quench the system to a temperature $T = 0.5J/k_B$. All the chains in the simulation are constructed to obey the *excluded-volume criterion*; i.e., any lattice site is not allowed to be occupied by more than one monomer at any given instant of time. The dynamics of the chains is mimicked by reptation and by kink-jump moves. The details of the dynamics used here can be found elsewhere.²¹ A trial move is rejected *immediately* if the excluded-volume criterion is not satisfied. Otherwise, the new state is accepted according to the usual Metropolis Monte Carlo sampling technique. After the system reaches equilibrium (monitored by the time dependence of the domain size), we compute, among other quantities, the spherically averaged static structure factor $S(k)$ and the real-space pair correlation function $G(r)$. The equilibrium domain size is calculated in the following way: Since the monomer concentration is fixed, the domain-size morphology in this system produces a damped oscillatory behavior in $G(r)$, for all values of N . This allows us to give a quantitative measure of the equilibrium domain size D_{eq} as the location of the first zero of the correlation function.

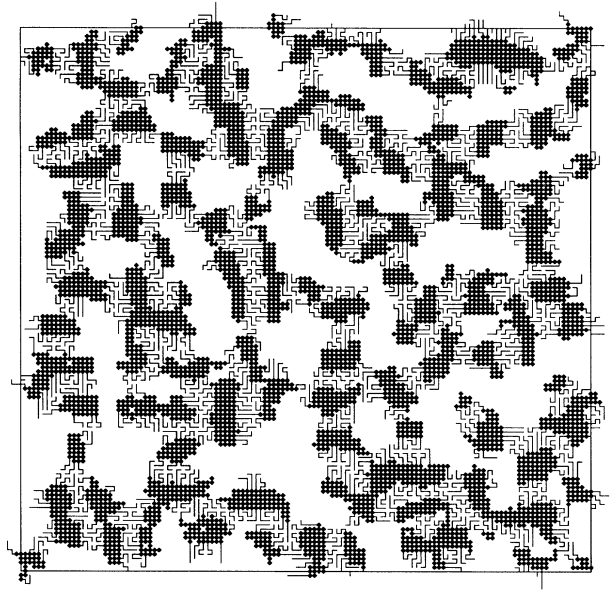


FIG. 1. A typical equilibrium morphology of the block-copolymer system for chain length $N=10$. For each chain, the two different blocks are denoted by connected lines and connected symbols, respectively. Even though we use periodic boundary conditions, the part of the chain outside the inner frame is drawn as it is in order to preserve the connectivity of the chains in the figure.

In the present lattice model of block copolymers, the segregation is weak even at final equilibrium stages; i.e., the interface thickness and the size of the microdomains are of the same order of magnitude. This seems clear from inspection of typical equilibrium morphologies of the domains (shown in Fig. 1 for chain length $N=10$). Although we cannot probe the experimentally more interesting strong-segregation limit (which would correspond to much larger chain lengths than considered here) due to the practical limitation on available computer time, we note that the cell-dynamics calculations^{8,9} are carried out in the weak-segregation case as well, and thus a test of possible universality in these two models is still within our reach.

In numerical studies of cell-dynamics models⁹ it was found that the equilibrium domain size scales as $N^{1/2}$ in the weak-segregation case. Since we want to test the possible universality between the cell-dynamics model and our microscopic model, we plot in Fig. 2 D_{eq} vs $N^{1/2}$. We find that the data are well represented by this power law, at least over the range of N values studied in this simulation, and thus $\theta = \frac{1}{2}$ in the microscopic model. Since universality of different models is usually characterized by the power-law exponent of some relevant measurable quantities, we conclude that these two models for block copolymers belong to the same universality class. This study also provides strong support towards the validity and applicability of the cell-dynamics models

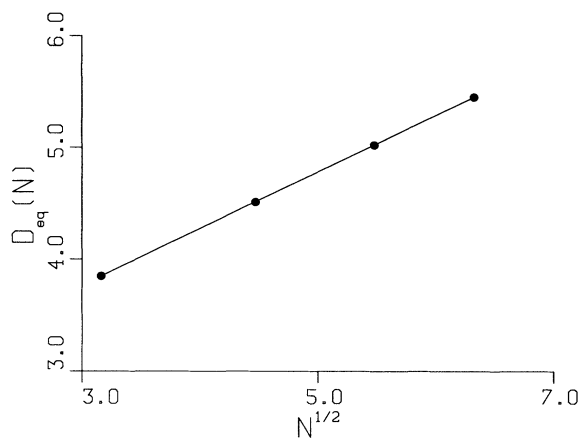


FIG. 2. The equilibrium domain size D_{eq} (see text) plotted against $N^{1/2}$ for various chain lengths. The straight line is the best fit to the data.

of block-copolymer melts.

In analogy with studies of spinodal decomposition in small molecular systems,¹³ we study the scaling behavior of the structure factor. Whereas in the case of spinodal decomposition, one studies a *dynamical* scaling, we prescribe a similar scaling *Ansatz* for the *static* N -dependent structure factor as

$$S(k, N) = D_{eq}^2(N) F(kD_{eq}(N)) \quad (2)$$

in two dimensions, where $F(\chi)$ is independent of the chain length. This scaling *Ansatz* is supported by the correspondence between the scaling properties of the equilibrium domain size of block-copolymer systems with that of the time-dependent domain size in the case of spinodal decomposition.⁹ We test the scaling *Ansatz* by plotting $S(k, N)/D_{eq}^2(N)$ vs $\chi = kD_{eq}(N)$ and checking whether the resulting functions are independent of the chain length. In Fig. 3 we show such a scaling plot. It seems from this figure that the scaling *Ansatz* of Eq. (2) works well for the chain lengths considered in this study. However, the scaling seems to improve with larger values of N and we expect that the quality of the scaling plot will improve considerably for asymptotically large chain lengths. It would be interesting to check whether the scaling functions for the continuum models agree with the ones calculated in the lattice model here, which would even strengthen the claimed universal behavior of the two models.

In summary, we have studied the scaling properties of a model of quenched block copolymers using Monte Carlo simulations. The simulations are carried out in two dimensions in the weak-segregation limit and the results are compared with those of a cell-dynamics-type continuum model also studied in two dimensions and for the same limit. Our results suggest that the present lattice model and the continuum model belong to the same universality class. However, we note that simulations of

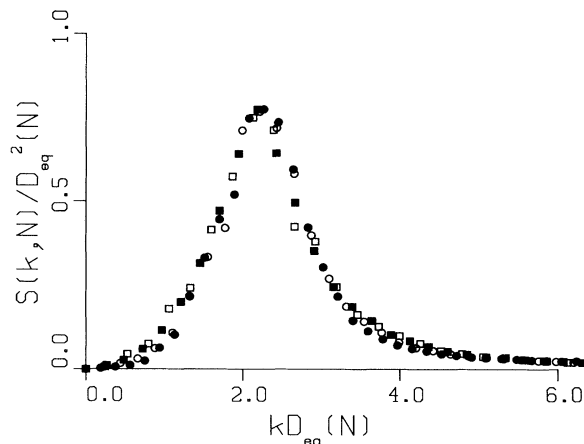


FIG. 3. The scaling *Ansatz* Eq. (2) (see text) is tested here by plotting $S(k, N)/D_{eq}^2(N)$ vs $kD_{eq}(N)$. The filled and open circles represent $N=10$ and $N=20$, respectively, and the filled and the open squares represent $N=30$ and $N=40$, respectively. Scaling seems to improve for larger N values.

the three-dimensional version of the present model are necessary to compare with real experimental situations, since one expects that the scaling function is different in three dimensions.

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