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Lamellar phase in a model for block copolymers

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We report results from a simulated annealing study of a coarse-grained model for block copolymers. For sufficiently slow cooling rate, the system develops a well-defined lamellar structure by avoiding the formation of defects. We show that the strong segregation limit of the model is computationally accessible when the interface thickness is small enough.

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In a block copolymer (BCP) melt, phase separation proceeds in a most interesting fashion [1,2] due to the special architecture of the polymer molecules comprising the melt. For example, consider a *di-block* copolymer melt that is composed of long chain molecules consisting of two covalently bonded subchains of constituent monomers of the A type and B type. If these two species are mutually incompatible, phase separation occurs at low temperatures. This phase separation, however, cannot proceed to a macroscopic scale due to the covalent bond between the A-type and B-type subchains. The state of the segregation is controlled by the product χN where χ is the A-B segment-segment Flory interaction parameter and N is the chain length. If χN is less than a critical value (typically of the order of 10), entropic factors dominate and the copolymer exists in a disordered state. On the other hand, an order-to-disorder transition takes place for larger values of χN. One finds that in the ordered state, the system can form periodic lamellar, spherical, or cylindrical structures, depending on the relative chain length of the two cobonded polymers. The distinctive properties of these structures have been attracting a lot of interest recently, due, in part, to the great technological importance of block copolymer materials. We will consider the *symmetric* case here, so that the ordered structure is given by a periodic lamellar mesophase. It has been found experimentally that the equilibrium mean thickness D of these microdomains scales with the molecular weight N of the copolymers as $D \sim N^{\theta}$. When the BCP system is in the ordered state but very close to the order-disorder transition point, it is said to be in the weak-segregation limit. This weak-segregation limit is characterized by a diffuse interface between the A and B lamellae, and experiments [3] in this limit yield $\theta=\frac{1}{2}$. On the other hand, for $\chi N \gg 10$, energetic factors dominate and the ordered domains are characterized by a very sharp interface and almost flat concentration profiles. In this case the system is in the strong-segregation regime and $\theta=\frac{2}{3}$ has been observed in experiments [4,5].

Theoretical studies of phase separation in block copolymers can also be divided in two general categories, dealing with the weak-segregation limit [6,7] and the strong-segregation limit [8–10], respectively. In the weak-segregation limit one usually neglects chain stretching, and mean-field theories in this limit correctly identify $\theta=\frac{1}{2}$. Since composition fluctuations play a major role near the order-disorder transition, applicability of these mean-field theories near such a critical point has been questioned recently [5,7,11]. Theories valid in the strong-segregation limit are reasonably successful in predicting domain structure and in particular a value of $\frac{2}{3}$ for the exponent θ.

We concentrate on a recently proposed phenomenological model [12–14] for the phase-separation dynamics of the block-copolymer system. In this model, one starts from a coarse-grained description of the ordering process in a similar fashion to the Cahn-Hilliard (CH) model [15] used to study phase separation in binary alloys. In the CH model, one writes down an order-parameter evolution equation in terms of a functional derivative of a coarse-grained free-energy functional, given usually by a Ginzburg-Landau expression. The fact that the equilibrium configurations in a block copolymer system are made out of microdomains is incorporated [12–14] by adding a long-range interaction in the model free-energy functional in the following way:

$$F[\phi]=\int d\mathbf{r}\left[-\frac{b}{2}\phi^2+\frac{u}{4}\phi^4+\frac{K}{2}|\nabla\phi|^2 +B\int d\mathbf{r}'G(\mathbf{r},\mathbf{r}')\phi(\mathbf{r}',t)\right], \tag{1}$$

where b, u, and K are usual parameters of the Ginzburg-Landau model and B is a new phenomenological parameter which characterizes the BCP system. In the above equation $G(\mathbf{r},\mathbf{r}')$ is the Green's function for Laplace's equation

$$\nabla^2 G(\mathbf{r},\mathbf{r}')=-\delta(\mathbf{r}-\mathbf{r}') \tag{2}$$

with a suitable boundary condition. Then, the evolution equation for the *conserved* order parameter [16] can be written down in a CH scheme [17] as

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

This equation is the same as the CH equation 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 [13,14] have studied a cell-dynamics [18] version of Eq. (3) in two dimensions in the weak-segregation limit. They empirically conclude that B is proportional to N^{-2} and on this basis find $\theta=\frac{1}{2}$. They have not been able to probe the strong-segregation limit of this model.

In this paper, we carry out a numerical study of the above model proposed by Oono and his group and demonstrate that the physically correct strong-segregation limit of the model is computationally accessible in two dimensions. However, it is important to note that in order to show this, we have had to use a simulated annealing technique, in order to form a well-defined lamellar structure. We find that when the interface thickness is small enough, the coarse-grained model yields the characteristic exponent for the strong-segregation case, whereas the weak-segregation exponent is achieved for a diffuse interface. We compute θ and find that when the interface is sharp enough, the strong-segregation limit can be reached, yielding a value of $\theta=\frac{2}{3}$, as seen in experiments.

Equation (3) can be written in a simpler form after rescaling [19] and the resulting equation reads

$$\frac{\partial\phi(\mathbf{r},t)}{\partial t}=\tfrac{1}{2}\nabla^2[-\phi+\phi^3-\nabla^2\phi]-\epsilon\phi\ , \tag{4}$$

where ϵ ($\sim N^{-2}$) is the only parameter of the model. We numerically integrate Eq. (4) by using a first-order Euler scheme in a two-dimensional lattice using a time step $\delta t=0.025$ and mesh size $\delta r=1$. We choose the initial values of ϕ to be uniformly distributed between -0.1 and 0.1 with the order parameter strictly equal to zero.

When quenched from such an initial configuration, the system shows ordering and the corresponding domain structure is shown in Fig. 1. This "labyrinthine" structure [20] coarsens a little bit as time passes but a well-defined lamellar structure does not arise even at a very late time. This type of behavior is seen in previous simulations by Oono's group and in experiments on block copolymers [2] and ferrimagnetic garnet films [20]. It has been suggested [13] that the situation might be different in three dimensions, since the interface is always rough in two dimensions. However, previous numerical studies in three dimensions [14,19] failed to find any ordered lamellar structures produced by sudden quenches. The disclination-type defects pin the system in the labyrinthine state also in three dimensions and this seems to happen in the presence of thermal noise as well [14]. In view of these results, Oono and Bahiana conclude that hydrodynamic effects must be important to obtain lamellar structure. They numerically study the effect of hydrodynamic interactions [14] in the formation of lamellar patterns in a Hele-Shaw cell and find that a symmetry-breaking flow field induces lamellar order.

We take a different approach. We realize that in order to straighten out the lamellae, transport of many polymer chains is necessary from that part of the system where the interface has a positive curvature. This becomes prohibitively difficult with only a diffusion mechanism at hand, once the microdomains are established. In order to allow the system to reorganize slowly into the lamellar phase while the ordering is still taking place, we carry out a simulated annealing procedure instead of a rapid quench. This simulated annealing mechanism is a well-known procedure [21] for obtaining the lowest-energy "ground states" in disordered systems [22,23]. Here, as an interesting application of this method, we use it to avoid the formation of defects. We add a thermal noise term in the evolution equation [Eq. (4)] in the form of $\sqrt{s}\,\eta(\mathbf{r},t)$, where s is the strength of the noise term [24]. We start with a large value of s ($s=0.5$), so that the system appears to be disordered [25] at this temperature. We anneal the system for a time of $t_a=2000$–4000 at each temperature and then reduce the noise strength each time by steps of $\delta s=0.025$. In such a slow cooling procedure the formation of defects is reduced and the system finally picks up the lamellar state as the ground state. Such a lamellar structure is shown in Fig. 2 for a 64^2 lattice with $\epsilon=0.01$. Even in this simulated annealing procedure, it is extremely time consuming to avoid formation of any defects when the system size is large and ϵ is small. Most of our results (at least for small values of ϵ) are thus confined to relatively small lattice sizes.

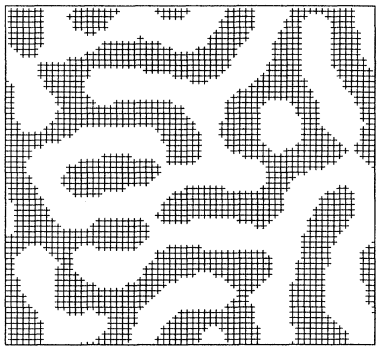

FIG. 1. A typical morphology of the block copolymer system after a rapid quench from high temperature for $\epsilon=0.01$.

We next turn to the question of evaluating the exponent θ for the lamellar structure. As we have mentioned earlier, Oono and his group found an exponent of $\theta=\frac{1}{2}$ from their numerical study. We would like to ascertain if the length scale is different when the lamellar structure is formed instead of the labyrinthine structure, and if this results in yielding the strong-segregation value for the exponent θ. Since defect structure in various systems [16,20,26] showing stripe patterns is of much recent interest, this sort of comparison of length scale can possibly elucidate the defect structure in related materials. When we compare the characteristic length, $R(\epsilon)$, of the patterns [27] in Figs. 1 and 2—where one structure shows a labyrinthine pattern and the other shows a lamellar pattern, we find that the characteristic length scale is not too different (the characteristic length is about 10% larger in the lamellar case) from one type of structure to

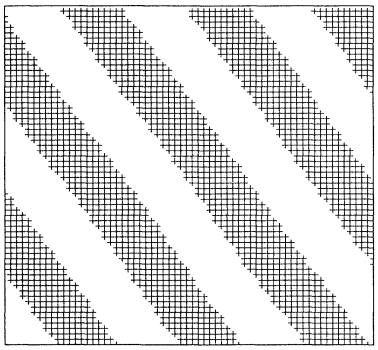

FIG. 2. The same system in Fig. 1 produces this well-defined lamellar structure by a simulated annealing procedure.

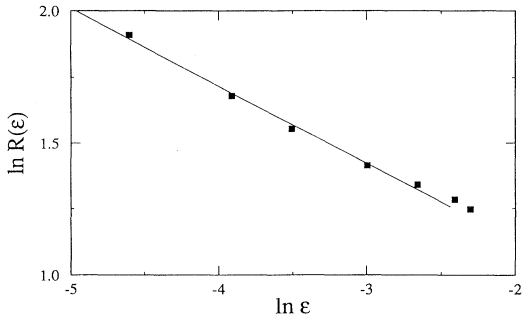

FIG. 3. A log-log plot of the characteristic length $R(\epsilon)$ vs ϵ. The slope of the straight line is given by -0.30 ± 0.02, which yields $\theta\approx0.60$. However, the magnitude of the slope is still increasing for smaller values of ϵ.

the other. This suggests that when quenched rapidly, the system acquires the length scale first and then tries to reorganize itself locally by getting rid of the defects.

In Fig. 3 we show a log-log plot of $R(\epsilon)$ versus ϵ. We find that the *overall* best fit to the data yields an exponent of -0.30 ± 0.02, which, using the identification $\epsilon\sim N^{-2}$, corresponds to $\theta\approx0.60$. This number is somewhat smaller than that expected for θ in the strong segregation limit. However, a straight-line fit to the last three points in Fig. 3 yields an exponent of 0.33, which translates into $\theta=\frac{2}{3}$. For these values of ϵ, the interface is sharp enough and the strong-segregation limit can be reached in the model calculation. Carrying out such a computation for even smaller values of ϵ will be quite interesting for confirming our results and for providing a totally definitive answer, but unfortunately such computations seem to be beyond reach at this point.

To conclude, we have carried out a simulated annealing study of a coarse-grained model of block copolymers and found that, for a sufficiently slow cooling rate, the system develops a well-defined lamellar structure by avoiding the formation of defects. We expect that this procedure will also yield well-defined lamellar structure in similar models with a nonconserved order parameter [16]. As noted earlier, we find that when the interface thickness is small enough, the coarse-grained model yields the characteristic exponent for the strong-segregation case, whereas the weak-segregation exponent is achieved for small values of the parameter ϵ. Such results for a one-dimensional version of the model considered here have been obtained recently [28]. One interesting question now is whether the model can display both the strong-segregation and weak-segregation limits as a function of temperature (or noise strength) for a fixed small value of ϵ. Another interesting question is how the defects creep in as the ordered lamellar structure melts by a reverse quench. These questions will be addressed in future publications.

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