Interface dynamics in a block copolymer melt and the effect of noise

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The role of fluctuations in the disorder-lamellar transition in a block copolymer melt is investigated using a cell dynamical system simulation by measuring the propagation velocity of the interface between ordered and disordered regions. Our results strongly suggest that near the transition temperature, in the absence of noise, the velocity increases with quench depth as $v \sim \sqrt{\tau}$ [$\tau = (T_c - T)/T_c$ is the reduced temperature measured from the transition temperature T_c], while in the presence of noise, the velocity increases as $v \sim \tau$. These results lead us to conclude that the addition of noise causes the disorder-lamellar transition to change from second order to first order. This conclusion is consistent with the prediction of Brazovskii [Sov. Phys. JETP **41**, 85 (1975)]. [S1063-651X(96)50606-9]

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Block copolymers (BCP's) are linear polymer chains, typically composed of two homopolymer subchains grafted covalently at one end. Their properties have attracted a great deal of interest, both scientific and technological. Depending on temperature and polymer composition, BCP systems have been found to exhibit many fascinating periodic structures as well as a homogeneous disordered phase. The mean field theories of Leibler [1], in the weak segregation regime, and Ohta and Kawasaki [2], in the strong segregation regime, yield phase diagrams which reproduce many features of phase diagrams obtained experimentally. According to these theories, the order parameter of the BCP system is introduced in the following way. Let $\phi_a(\boldsymbol{r})$ and $\phi_b(\boldsymbol{r})$ denote the local volume fractions of a and b segments, and N_a and N_b represent the degrees of polymerization of a and b blocks. Under the condition that the molten phase is incompressible [$\phi_a(\boldsymbol{r}) + \phi_b(\boldsymbol{r}) = 1$], the system can be described by a single order parameter: $\psi(\boldsymbol{r}) = \phi_a(\boldsymbol{r}) - \phi_b(\boldsymbol{r})$. The spatial average of $\psi(\boldsymbol{r})$ is given by $\psi = 2f - 1$, where f is the block ratio, $f = N_a/(N_a + N_b)$.

According to Leibler's mean field theory, for a symmetric chain [$N_a = N_b$], the transition from a disordered system to an ordered system is second order, and the resulting ordered phase consists of alternating ''stripes'' (lamellae) of a-rich and b-rich regions. Systems which exhibit such a transition between a homogeneous isotropic disordered phase and a lamellar phase belong to the ''Brazovskii universality class'' [3]. For such systems, the transition to the ordered state, predicted to be second order by mean field theory, is expected to become first order due to the effect of fluctuations. Treating fluctuations within the Hartree approximation, Fredrickson and Helfand calculated the phase diagram for the BCP system and obtained results significantly different from those obtained within the mean field theory [4]. Some of their predictions have been confirmed experimentally [5].

In this article, we investigate the effects of fluctuations on a symmetric BCP system through computer simulation by studying the propagation velocity of the interface between the lamellar phase and the disordered phase near the transition temperature. It should be noted that the system we study presents special technical problems. The only work of which we are aware concerning the identification of a fluctuation-induced first order transition in a numerical simulation was recently reported by Shiwa *et al.* [6]. Using a cell dynamical system (CDS) approach [7] to study the Swift-Hohenberg equation, they found a double-plateau evolution of the Nusselt number in the presence of noise.

Perhaps the most direct method to distinguish a first order transition from a second order transition is to consider the evolution of droplets of the equilibrium phase in the parent phase, that is, to determine if sufficiently small droplets will shrink and eventually disappear rather than grow. (Of course, in this case, it is never possible to make a certain identification of a second order transition.) For the present case, however, such a study is not practically feasible. The system we study is very close to the critical temperature. In general, if both phases appear in such a system, their interface will extend over a very long distance. (The thickness of the interface is essentially the correlation length of the system.) If we place a single small droplet of the equilibrium phase in a system prepared in the parent phase, its dynamics will initially be dominated by diffusion, and it will quickly spread and its amplitude shrink. In a noiseless system, this would not prevent us from determining the fate of this droplet. Its evolution could be followed indefinitely, and its amplitude would eventually be seen to everywhere approach zero or its equilibrium value. However, to investigate the behavior in

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which we are interested, we must add noise to the system. In this case, when we place a localized droplet of the ordered phase in the disordered phase, its amplitude quickly decays, and it becomes ''lost'' in the noise. Its subsequent evolution cannot be distinguished from the evolution induced by the noise. The time development of the droplet thus cannot be isolated, and it cannot be said to either ultimately shrink and disappear or to grow.

Even in the system we study, it is possible in principle to study the evolution of droplets, but in order to do so, they must extend over a region whose size is on the order of the correlation length. With the parameter values used in the present numerical study, and using results appearing in Ref. [8], this length was found to be between approximately 1000 and 2000 cells. It may be thought that in such a situation, it would be possible to simply coarse-grain the system so that the correlation length corresponds to any desired reasonably small number of cells. However, in the present case, this cannot be done since coarse-graining beyond a certain point will result in the period of the ordered structure becoming smaller than the cell size. For the parameter values we consider here, the period of the ordered structure is approximately 25 to 50 times shorter than the correlation length. Thus to honestly study the dynamics of droplets for the present purpose would require a system size of perhaps at least 2000×2000 (approximately 60 times larger than the system used in our investigation) and a somewhat tedious preparation of the initial droplets. In a system such as this, a metastable disordered state cannot be distinguished from an unstable disordered state through a study of local dynamics. In this sense, we can say that locally there is no difference between the two. Only when we consider more macroscopic behavior can the distinction between the two be made, and in this sense, only here does the distinction have meaning.

Another method which could be used to identify a first-order phase transition is to measure the scattering function of the equilibrium pattern in the neighborhood of the transition temperature and look for a discontinuity in the scattering peak height. We attempted this, but were unable to detect any such discontinuity. Evidently, the precision of our numerical computation was not sufficient.

The method we use in this study relies on the fact that the temperature dependence of the steady state propagation velocity of an interface separating the disordered and ordered phases directly reflects the order of the transition [9,10]. In the case of a second order transition, the steady-state velocity of an interface separating the stable ordered state and the unstable disordered state depends on the velocity in accordance with the relation $v\sim\sqrt{\tau}$ [$\tau=(T_c-T)/T_c$, T_c is the transition temperature], provided fluctuations and initial inhomogeneities are sufficiently small [11]. In the case of a first order transition, the interface velocity in the steady state depends linearly on the temperature near T_c [9]. By performing a CDS simulation for the BCP system, we have carried out a dynamical test of the BCP system to determine how fluctuations affect the nature of the phase transition. In fact, an earlier investigation of the type of phenomena in which we are interested was carried out experimentally in a liquid crystal system near the nematic–smectic-*A* transition by Cladis *et al.*, whose results strongly suggest that this transition is weakly first order [9,10]. A similar experiment for BCP systems is also important not only to determine the order of the transition but also to test the various properties of front propagation in such systems and compare these with the corresponding theoretical predictions.

Oono and Shiwa proposed the following partial differential equation to describe the dynamics of microphase separation in a BCP system (with no macroscopic flow) [12]:

$$\frac{\partial\psi}{\partial t}=\nabla^2[-D\nabla^2\psi-a\psi+u\psi^3]-B[\psi-\overline{\psi}], \tag{1}$$

where ∇^2 is the Laplacian, and B, D, a and u are positive phenomenological parameters. The term proportional to B reflects the long range interaction. On the basis of this equation, the problem of front propagation in a BCP system was studied numerically by Liu and Goldenfeld for a symmetric one-dimensional system [13]. The value of the selected front velocity they determined agrees with that derived using the marginal stability conjecture [11]. Later, employing the reductive perturbation method, one of the present authors (G.P.) studied the invasion of lamellar, triangular and bcc ordered phases into the disordered region and calculated propagation velocities of front-envelope profiles for various invasion processes near the spinodal line [8].

A CDS model corresponding to Eq. (1) in the presence of noise was also introduced by Oono and Shiwa [12] as a slight modification of the CDS model describing spinodal decomposition. A detailed investigation of this system was subsequently performed by Bahiana and Oono [14]. We employ the same CDS model, where the difference equation for the order parameter ψ is given by

$$\psi(\boldsymbol{n},t+1)=\psi(\boldsymbol{n},t)+\langle\langle\mathcal{I}(\boldsymbol{n},t)\rangle\rangle-\mathcal{I}(\boldsymbol{n},t)-\mathcal{B}[\psi(\boldsymbol{n},t)-\overline{\psi}]+\mathcal{C}\eta(\boldsymbol{n},t), \tag{2}$$

with

$$\mathcal{I}(\boldsymbol{n},t)=-\mathcal{D}[\langle\langle\psi(\boldsymbol{n},t)\rangle\rangle-\psi(\boldsymbol{n},t)]-\mathcal{A}\tanh\psi(\boldsymbol{n},t)+\psi(\boldsymbol{n},t), \tag{3}$$

where $\boldsymbol{n}=(n_x,n_y)$ designates the two-dimensional lattice point (n_x and n_y are integers). We choose the units of length and time in a such way that the lattice constant and the transport coefficient do not appear in the above equations. The quantity $\langle\langle X\rangle\rangle$ is an isotropic spatial average, defined on the square lattice by $\langle\langle X\rangle\rangle=(1/6)\Sigma X$(nearest-neighbor cells) $+(1/12)\Sigma X$(next-nearest-neighbor cells). Hence the correspondence between the coefficients in Eq. (1) and the above equations is $a=\mathcal{A}-1$, $B=3\mathcal{B}$, $D=\mathcal{D}/3$. Time t is also scaled by factor of 3. The last term in Eq. (2) represents the noise; $\mathcal{C}$ is the noise amplitude, taken here as an independent parameter [15] and $\eta(\boldsymbol{n},t)=\eta_x(n_x+1,n_y,t)-\eta_x(n_x,n_y,t)+\eta_y(n_x,n_y+1,t)-\eta_y(n_x,n_y,t)$, where η_x and η_y are random numbers uniformly distributed in the interval $[-1,1]$. In our simulations, we fixed the parameters as $\mathcal{B}=0.02$, $\mathcal{C}=0$ or 0.01, $\mathcal{D}=0.5$, $\overline{\psi}=0$, and varied $\mathcal{A}$ around the transition temperature $\mathcal{A}_c$.

Linear stability analysis of Eq. (1) shows that the spinodal line is determined by $(a-3u\overline{\psi}^2)^2-4BD=0$ [8]. Since the microphase-separation temperature (MST) and the spinodal temperature coincide for the symmetric, $\overline{\psi}=0$ case, the tran-

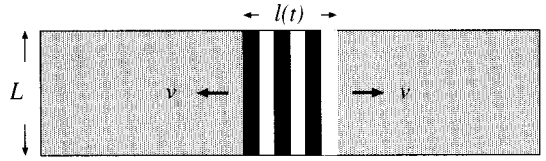

FIG. 1. Schematic representation of the invasion of a lamellar phase into a homogeneous disordered phase.

sition temperature between the lamellar and disordered phases is $a_c=2\sqrt{BD}=2\sqrt{\mathcal{B}\mathcal{D}}=0.2$ for the above parameter values. Hence the corresponding critical value of $\mathcal{A}$ in Eq. (3) for $\psi=0$ is $\mathcal{A}_c=1+0.2=1.2$.

In order to examine the velocity of the propagating interfaces, we first produced sufficiently developed (30 000 time steps) ''seed'' patterns on a square lattice of size 128×128 for various values of $T<T_c$ ($\mathcal{A}>\mathcal{A}_c$) near the transition point. Then the ''seed'' patterns were mounted in the middle of lattice of size 128×512 with periodic boundary conditions. Having prepared such an initial state, we allowed the interface to propagate with the same value of $\mathcal{A}$ as that with which the ''seed'' pattern was produced. In contrast to the real system, however, the above CDS model with $\psi=0$ does not produce a well-defined lamellar structure, but rather a complicated bicontinuous pattern. Bahiana and Oono attempted to avoid this difficulty by performing a three-dimensional simulation, adding thermal noise, imposing a bending penalty, and taking into account hydrodynamic interactions, but none of these attempts changed the pattern significantly [14]. We have found that a well-ordered lamellar structure can be obtained by imposing a macroscopic shear flow, the velocity of which is given by $v_x(\boldsymbol{r})=\dot{\gamma}y$ and $v_y=v_z=0$. In this case, the right-hand side of Eq. (1) acquires the convective term $-\dot{\gamma}y(\partial\psi/\partial x)$, and a corresponding discretized term appears in Eq. (2). It should be stressed, however, the shear flow was applied only during the preparation of the ''seed'' patterns and was turned off when we measured the interface propagation velocity.

Recently, the nucleation of a lamellar phase in a fluctuation-induced first order transition was discussed by Hohenberg and Swift [16]. They showed that the critical droplet shape is anisotropic in general. In their terminology, the subject of the present investigation is the propagation of a ''longitudinal'' interface, as shown in Fig. 1. In the calculation of the interface velocity, the front position was specified for every ten time steps by measuring the total length of the ordered region. The length $l(t)$ of the ordered region was estimated by the value $l(t)=2\Sigma\psi(\boldsymbol{n},t)^2/L\psi_{max}^2$, where ψ_{max} is the maximum value of $\psi(\boldsymbol{n})$, and L is as shown in Fig. 1. In the presence of noise, an average over more than ten propagations was taken. While there are obvious problems with this method of calculating the velocity (especially in the presence of noise), for the present problem, we feel it is probably the most precise method which can be realized using a relatively simple numerical procedure, as long as lk_0 is not too large, where k_0 is the wave number of the equilibrium ordered pattern. Fortunately, we were able to obtain meaningful results using a small enough number of time steps that lk_0 never became larger than approximately 10. For values of $\mathcal{A}$ very close to $\mathcal{A}_c=1.2$ (approximately 1.202 and less), the propagation velocity was not large enough to obtain meaningful results using our numerical procedure.

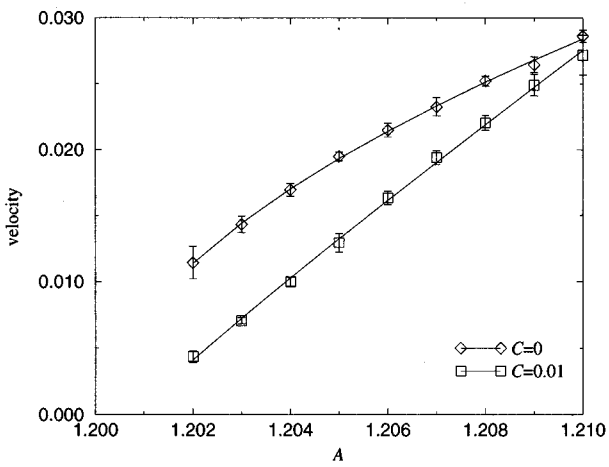

FIG. 2. Propagation velocity for the invasion of a lamellar ordered region into a disordered region in the absence and presence of noise.

We first discuss the noiseless system, i.e., $\mathcal{C}=0$. In Ref. [8], the propagation velocity v is calculated using the reductive perturbation method as

$$v=[2a(a^2-4BD)/D]^{1/2}. \tag{4}$$

If we consider the temperature just below T_c, we put $a=a_c+\tau=2\sqrt{BD}+\tau$ ($a_c\gg\tau$, $\tau>0$), and hence $v\sim\sqrt{\tau}$ to lowest order in τ. In terms of $\mathcal{A}$, we have $v\approx0.327\times(\mathcal{A}-1.2)^{1/2}$ for the above parameter values. In Fig. 2, the propagation velocity v determined through our numerical simulations is plotted as a function of $\mathcal{A}$. As shown, the data are fit well by the curve $v=0.345\times(\mathcal{A}-1.20)^{0.540\pm0.005}$. If the point at $\mathcal{A}=1.210$ is removed from the fit, we obtain $v=0.306\times(\mathcal{A}-1.20)^{0.513\pm0.006}$. For a range of values of $\mathcal{A}$ infinitesimally close to $\mathcal{A}_c$, the exponent appearing here should be exactly 1/2. As the maximum value of $\mathcal{A}$ increases, however, this value should also increase [as seen by expanding Eq. (4) to second order]. Our results are consistent with this behavior.

We now study the effect of the noise for the case $\mathcal{C}=0.01$. This value was also used in Ref. [6]. In this case, the lamellar pattern develops spontaneously in the region ahead of the front. To minimize the error introduced by the presence of this ''undesired'' order, in the calculation of $l(t)$ we removed the contribution of $\psi(\boldsymbol{n})^2$ for values of $\boldsymbol{n}$ for which the deviation from zero had not been caused by the front. Of course, this procedure itself is inherently error-ridden, but it is perhaps the best alternative. After a sufficiently long time, the propagation of the front is impeded significantly by the spontaneously developed ordered phase growing before it. We determined the propagation velocity before this ''collision'' occurs, and the result is also shown in Fig. 2. The data are fit well with the curve $v=2.27\times(\mathcal{A}-1.20)^{0.938\pm0.015}$ given in the figure. Again if we remove the point at $\mathcal{A}=1.210$ from the fit, we obtain $v=3.05\times(\mathcal{A}-1.20)^{1.005\pm0.013}$. As in the noise-free system, we expect that the observed deviation from 1 in the former

case is due to the presence of a non-first-order contribution. (Note in this case, the second-order effect should cause the exponent to decrease.) We believe that our result reflects the first order nature of the transition due to the Brazovskii effect. We point out that our result is consistent with the calculation of the growth kinetics of a BCP lamellar droplet by Fredrickson and Binder in the sense that v is proportional to τ [17]. As mentioned above [16], however, their assumption of a spherical droplet is problematic since, as discussed in Ref. [8], the propagation velocity of the front is highly anisotropic. An investigation using other values of the noise amplitude is presently underway, and the details of our results will be published elsewhere. The predicted effects of shear flow on the Brazovskii type transition [18] will also be investigated in the future.

In summary, within the CDS approach, we found evidence of a fluctuation-induced first order transition in a symmetric BCP system by measuring the velocity of the interface between the ordered and disordered phases.

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