I. INTRODUCTION

Nonequilibrium phenomena encountered in physical, chemical, and biological systems represent a most exciting research topic. The formation of static and dynamic patterns, spatial-temporal chaos, and fractal growth phenomena are only three of a number of interesting areas connected to this field of physics.\(^1\) As an example, the investigation of nonequilibrium phenomena in the polymeric system, especially in the diblock copolymer (DBCP) systems, has opened new prospects because of their complexity and distinctive phase behavior.\(^2\)\(^3\) A DBCP is a synthetic molecule composed of two homopolymer subchains A and B jointed covalently at one end. At the copolymer melt state, of which temperature is above the critical temperature \(T_c\), A and B mix completely. Below \(T_c\), if the two subchains are not compatible with each other, the copolymer undergoes mesoscopic phase separation. However, on account of the covalent bond joint of A and B, macrophase separation is not possible to take place, and such a copolymer, in equilibrium below \(T_c\), will thus form A- and B-rich mesoscale domains. When mesoscale phase separation occurs, the resulting equilibrium structure is regular and periodic rather than random.\(^2\) Nonetheless for the phase separation induced by usual homogeneous quenching, the macroscopic arrangement of these mesoscopically ordered domains is random. In recent years, it was found experimentally that different orientations of the lamellar normal can be selected by applying some external symmetric breaking field, such as steady shear flow,\(^4\) oscillatory dynamic shear,\(^5\)\(^6\) roll-casting,\(^7\) and geometric constraints.\(^8\)

It is interesting to ask what will happen if the phase separation of DBCP is induced by a spatial-temporal inhomogeneous quenching? The simplest example could be of cooling the thin film of DBCP from one end, which can be considered as a symmetric breaking external field. We would expect that the appearance of a segregation pattern invades the featureless disordered phase at the quench boundary between stable and unstable phases if the temperature boundary moves slowly. This front propagation in a DBCP system was first investigated by Liu and Goldenfeld,\(^9\) who numerically studied the invasion of a macroscopically ordered phase getting into an unstable disordered phase in a symmetric (equal length subchain) one-dimensional system. Within the weak segregation limit, Paquette\(^10\) studied the dynamics of front propagation in a DBCP system based on the model equation deduced by Oono and Shiwa\(^11\) and found out that the ordered pattern of the front will form a superposition of different
II. EQUATION OF MOTION AND SIMULATION

The dynamics of phase separation in a DBCP melt can be described by the partial differential equation

$$\frac{\partial \Psi(r,t)}{\partial t} = M \nabla^2 (-D \nabla^2 \Psi - A \tanh \Psi + \Psi) - M \alpha (\Psi - \bar{\Psi}),$$

where $f = N_A / (N_A + N_B)$ is the molecular weight ratio of subchain A, $N_A$ and $N_B$ are the chain lengths of blocks A and B, respectively. $\Psi(r,t)$ is the scalar order parameter chosen to be $\varphi_A(r) - \varphi_B(r)$, where $\varphi_A(r)$ and $\varphi_B(r)$ are the reduced local volume fractions of components A and B, respectively. $M$ is the mobility, $\alpha = [(N_A + N_B) b f (1 - f)]^{-2}$ with $b$ the Kuhn’s statistical segment length and $D = b^2$. $A$ is a phenomenological parameter inversely proportional to the temperature. $\Psi$ is the molecular composition and is defined as

$$\bar{\Psi} = \int d\mathbf{r} \, \Psi(\mathbf{r}) = 1 - 2f.$$

Equation (1) can be derived from a Ginzburg–Landau free energy, using the phenomenological time-dependent Ginzburg–Landau (TDGL) equation for a conserved order parameter. Neglecting the random thermal noise, it can be written as

$$\frac{\partial \Psi(r,t)}{\partial t} = M \nabla^2 \frac{\delta F\{\Psi(r,t)\}}{\delta \Psi(r,t)},$$

with the free-energy functional,

$$F\{\Psi\} = \frac{1}{V} \int_v \left[ \frac{D}{2} (\nabla \Psi)^2 - \frac{\tau}{2} \Psi^2 + \frac{b}{4} \Psi^4 \right] dv + \frac{\alpha}{2V} \int_v dv \int_v dv' \, G(\mathbf{r},\mathbf{r}') \left[ (\Psi(\mathbf{r}) - \bar{\Psi}) [ (\Psi(\mathbf{r}') - \bar{\Psi}) \right],$$

where $V$ is the volume of the system and $G(\mathbf{r},\mathbf{r}')$ is the Green’s function for Laplace’s equation

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

with appropriate boundary conditions. $D(\nabla \Psi)^2$ is the interfacial free-energy. The free-energy functional, Eq. (4), essentially the effective Hamiltonian is first derived by Leibler and further discussed by Ohta and Kawasaki for a DBCP system. It implies that the chain length of DBCP considered here is long enough and the phase separation temperature is far away from the critical temperature, so that the fluctuation corrections to mean-field theory discussed by Frederickson and Helfand are negligible. The parameter $\tau = (A - 1)$ in Eq. (4) can relate to the Flory–Huggins parameter $\chi$ through

$$\tau = 8f(1 - f) \rho_0 \chi \frac{2s(f)}{f (1 - f) N},$$

where $\rho_0$ is the monomer number density, $N = N_A + N_B$ is the total length of the DBCP chain and $s(f)$ is a constant of order unity. The second term in $F$ represents the long-range interaction of $\Psi(\mathbf{r})$ due to the connectivity of different chemical sequences in a DBCP.
Equation (1) is simulated by the cell-dynamics system (CDS) method on a square lattice of size 100×100. In the CDS, Laplacian can be expressed as

$$\nabla^2 \Psi \to \langle \langle \Psi \rangle \rangle - \Psi,$$

where $\langle \langle \Psi \rangle \rangle$ represents the average over all the neighbors of lattice $r$. In the case of a two-dimensional system,

$$\langle \langle \Psi(r,t) \rangle \rangle = \frac{1}{6} \sum_{r_i, r_{iN}} \Psi(r',t) + \frac{1}{12} \sum_{r_i, r_{iNN}} \Psi(r',t),$$

where $NN$ and $NNN$ represent the lattice sites of nearest-neighbors and next-nearest-neighbors, respectively. Then Eq. (1) can be discretized in a form

$$\Psi(r,t+1) = \Psi(r,t) + M\{ \langle \langle I(r,t) \rangle \rangle \}
- I(r,t) - \alpha [\Psi(r,t) - \bar{\Psi}],$$

with

$$I(r,t) = [-A \tanh \Psi(r,t) + \Psi(r,t)] - D[\langle \langle \Psi(r,t) \rangle \rangle - \Psi(r,t)].$$

Although Eq. (9) is a discretized kinetic equation, the spatio-temporal change of order parameter is smooth.

The structure factor is defined by

$$S(k,t) = \langle |\Psi(k,t)|^2 \rangle,$$

which provides us with rich information and is directly observed in scattering experiments. In Eq. (11), $\langle \cdots \rangle$ represents the average of the whole system. The linearized treatment for a homogeneous quenching of a DBCP gives the following evolution function of the structure factor:

$$S(k,t) = S(k,0) \exp(-2MT_\perp t),$$

with the $k$-dependent growing coefficient,

$$\Gamma_\perp = Dk^4 - \pi k^2 + \alpha.$$

As pointed out by Furukawa, when the quenching is done from a single phase far from the critical point, we may assume that $S(k,0) =$ constant. Then the time evolution of the structure factor exhibits several important characteristics.

(i) $S(k,t)$ has a single peak at a constant wave number. It corresponds to the microscopic length scale $\lambda_m$,

$$k_m = \left( \frac{\tau}{2D} \right)^{1/2}, \quad \lambda_m = \frac{2\pi}{k_m} = 2\pi \left( \frac{2D}{\tau} \right)^{1/2}. \quad (14)$$

(ii) The peak height of the structure factor exhibits an exponential growth, Eq. (12). We have a microscopic time scale, $t_c$, defined by

$$t_c = [2M(-DK_m^4 + \pi k_m^2 - \alpha)]^{-1}. \quad (15)$$

These length and time scales are important natures of the discretization of the spatial-temporal structures. Namely $\lambda_m$ must be much larger than the lattice spacing $|\Delta r|$, which is set to unity in CDS; and the time interval $\Delta t$, which is also set to unity in CDS, must be much shorter than $t_c$. For this purpose we set $M$ to unity and apply Fourier analysis to Eq. (9). Then we have

$$\Psi(k,t+1) = \Psi(k,t) - \Lambda k^2(-D\Lambda k^2 - \tau)\Psi(k,t) - \alpha \Psi(k,t), \quad (16)$$

with

$$-\Lambda k^2 \equiv \frac{1}{2}(\bar{n} \cdot \bar{n})^2, \quad |\bar{n}| \equiv 1, \quad (17)$$

where $\bar{n}$ is the vector denoting the neighboring sites. We employ a spherical averaged value of $\Lambda$. In two-dimensional square lattice, $\Lambda$ is about a quarter. In the case of $D=0.5$, $\tau=0.35$, $M=1$, and $\alpha=0.02$, $D$ and $M$ in Eqs. (14) and (15) should be replaced by $\Lambda M=1/4$, $\Lambda D=1/8$. Then we have

$$\lambda_m \approx 5.3, \quad \text{lattice spaces}, \quad (18a)$$

$$t_c \approx 35.6, \quad \text{iterations}, \quad (18b)$$

$$v_0 = \frac{\lambda_m}{t_c} \approx 1/6.7, \quad \text{lattice space/iterations}, \quad (18c)$$

where $v_0$ is the minimum quench front velocity whose instability is triggered by the phase boundary. Therefore, we found that the CDS with chosen parameters meets the conditions of Eqs. (14) and (15), i.e., $\lambda_m \gg |\Delta r|$ and $t_c \gg \Delta t$. With the above choice, in the case of usual homogeneous quenching, we obtain the lamella thickness of 5 to 6 lattice spaces for $f=0.5$ and sphere diameter also of 5 to 6 lattice spaces for $f=0.4$, which agrees with the empirical formula, $l=\alpha^2$ with $\alpha=-0.256 \pm 0.003$, quite well.

The directional quenching in this simulation is realized by the following various external conditions. Let us consider a homogeneous DBCP system. We set a quench boundary that distinguishes the system into two parts: stable and unstable phases. This may be set by changing temperature: In one phase the temperature is set lower than the critical one ($\tau=0.35$ in this study) and in another phase it is set higher ($\tau=0.05$ in this study). The boundary width between two parts is one lattice space in this study. When the quench boundary is fixed the system stays in equilibrium. The boundary shift is realized as follows. The time is measured in discrete steps as $t=0, 1, 2, \ldots \text{[iterations of Eq. (1)]}$ in the CDS scheme. The quench boundary is shifted for one lattice space in each set of $n (n=1, 2, \ldots)$ steps of time. The quench boundary velocity is therefore $v=1/n$, (lattice/iterations), where the lattice space constant is set to unity in the CDS scheme. Just after the quench we prepared an unstable region with width of five lattice spaces, and then we shift the quench boundary. When one part of the stable phase comes into the unstable region, $\Psi$ is randomly set $\Psi(r)=\Psi \pm \delta\Psi_0$, where $\delta\Psi_0$ is the initial amplitude of the order parameter disturbed by the thermal fluctuations. In this simulation $\delta\Psi_0$ is varied from 0 to 0.1, which is generated by uniformly distributed random numbers, to study the stability of the invading front to the thermal fluctuation. We have also used the Gaussian distributed random numbers in the simulation and the results are essentially the same. The $\Psi(r,t)$ of the system evolves following Eq. (1). In order to quantitatively examine the macroscopic anisotropy of domain arrangement quantitatively, we define the deformation factor $\epsilon$ to describe the orientation of lamellae.
To calculate the deformation factor, we use the hardened order parameter, $\Phi = \text{sign}(\Psi) = \pm 1$, and the number of nearest-neighbor pairs of different signs of hardened order parameter. First we calculate the numbers of pairs of boundary sites in horizontal and vertical directions, $B_h$ and $B_v$. Then we calculate the deformation factor as follows:

$$
\varepsilon = \frac{B_v}{B_v + B_h} - 1. \tag{19}
$$

It is obvious that the perfect regular column morphology (lamellar normal is perpendicular to the normal of quench boundary) will result in $\varepsilon = -1$, the perfect regular lamellar morphology (lamellar normal is parallel to the normal of quench boundary) will result in $\varepsilon = 1$ and macroscopically random arrangement of lamellae gives $\varepsilon = 0$. We should mention here that the deformation factor defined by Eq. (19) is not sensitive for distinguishing the irregular triangular and regular triangular phases.

III. SIMULATION RESULTS AND DISCUSSIONS

A. Lamellar phase morphologies under directional quenching

For symmetric DBCP ($f=0.5$), the average order parameter $\Psi = 0$, and it produces lamellar phase morphology without macroscopic order of lamellae in homogeneous quenching. In the case of directional quenching, similar to that of polymer blends, the irreversibility (i.e., the degree of nonequilibrium) is measured by the reduced shift velocity of the quench boundary. The typical domain morphologies for a two-dimensional DBCP system with various shifting velocities of quench boundary are shown in Fig. 1. It is quite clear that the instability is triggered by the (initial) thermal fluctuation in the homogeneous quenching. However, the selection of the unstable mode in directional quenching depends on how fast the quench boundary passes over. Besides the thermal fluctuation trigger, the instability is also triggered by the front propagation resulted from the mismatch in the order parameter at the phase boundary between the phase-separating part and just-quenched part. Following Eqs. (14), (15), and (18), we know that the instability propagates with the velocity $v_0$ in the homogeneous unstable phase. Consequently, when the order parameter at certain lattice in the homogeneous unstable system changes by an amount $\partial \Psi$, this amplitude tends to increase. This increase is realized by mutual diffusion between that lattice and its surroundings, i.e., by changing the order parameters of the neighboring lattices. Therefore, the instability propagates in space with the velocity $v_0$, which has been evaluated by dimensional analysis and gives $v_0 = \lambda_g/\ell_c$.\(^{13}\) One important characteristic of homogeneous quenching is that the instabilities triggered by thermal fluctuation from different directions interfere with each other. Thus, the lamellae formed by homogeneous quenching are macroscopically isotropic and termed as irregular lamellar morphology (ILM), Fig. 1(e). In contrast to that, the instability triggered by the propagation front, i.e., the phase boundary, is directionalized and propagates for long distance until the thermal fluctuation increases and smears out the directionalized perturbation. The results indicate that the random instability is effective for fast shifting of the quench boundary, whereas the directionalized instability is effective for slower shifting of the quench boundary. The limiting case is that the thermal fluctuation is almost completely ineffective when the quench boundary is shifting very slowly. In this quasistatic case, the phase separation occurs so as to minimize the total free-energy, especially the quench boundary free-energy. In this way the phase pattern corresponding to the minimum of the interfacial energy between phase-separating part and just-quenched part will be selected. Therefore, we will see that the regular column morphology (RCM) is obtained for very slow quench boundary shift velocity, Fig. 1(d). The three-dimensional view of the deformation factor $\varepsilon$ defined in Eq. (19) for different (initial) thermal fluctuations at various quench boundary shifting velocities is shown in Fig. 2(a). The projection onto the $\partial \Psi/\Psi - 1/v$ plane gives the phase diagram of the domain morphology, Fig. 2(b). In the paper following, we will discuss it in detail.

1. Irregular lamellar morphology (ILM)

When the quench boundary velocity $v_0 > \nu_a$, where $\nu_a$ is some critical value, the situation is essentially equivalent to the homogeneous quenching, Fig. 1(e), though the time lag exists from position to position along the quench boundary shifting direction. The pattern generated is an irregular lamellar morphology (ILM) which is corresponding to the case of $\varepsilon < 0$, Fig. 1(a). It indicates that the regular perturbation from the quench boundary is not effective, or it can not compete with the perturbation of random (initial) thermal fluctuation, when $v_0 > \nu_a$. Therefore, the value of $\nu_a$ depends on the amplitude of (initial) thermal fluctuation. The only difference from the directional quenching of polymer blends is that the lamellar thickness in DBCP is well defined and is determined by the value of $\alpha$, while the characteristic domain size of the bicontinuous morphology of the spinodal decomposition of polymer blends can grow up continuously as long as the time keeps going on.

2. Regular lamellar morphology (RLM)

When the quench boundary velocity $v_i < \nu < \nu_a$, where $\nu_i$ is a smaller critical velocity, the instability will be triggered both by (initial) thermal fluctuation and the directional propagation front from the edge of the phase that has already started phase separation. The regular perturbation induced by quench boundary will propagate with the velocity defined by Eq. (18) when the (initial) fluctuation does not exist. However, in the presence of thermal fluctuation, the domain morphology becomes irregular whenever $\nu > \nu_i$, Fig. 1(a). This indicates that the regular perturbation can not compete with the irregular perturbation when $\nu > v_i$. When the quench boundary velocity $v_i < \nu < \nu_a$, the order parameter gradient across the quench boundary is small compared with that at the edge of the quenched phase-separating phase. This regular perturbation causes the coarsening of the domain along the quench boundary and tends to yield a regular morphology in which the lamellar interfaces are parallel to the
FIG. 1. Typical domain morphologies at various quench boundary shifting velocities. The initial order parameter fluctuation $\delta \Psi_0 = 0.05$ and the model parameters are: $f = 0.5$, $D = 0.5$, $\tau = 0.35$, $M = 1$, and $\alpha = 0.02$. (a) $1/\nu = 9$; (b) $1/\nu = 15$; (c) $1/\nu = 25$; (d) $1/\nu = 35$; (e) homogenous quenching. The quench boundary is shifting downwards.
where \( l_{\text{max}} \) is the maximum distance within which the regular perturbation is effective. The final result obtained by Furukawa\(^\text{13}\) is

\[
V_a = \min \left[ C_0 \ln \left( \frac{\Psi_s}{C \delta \Psi_0} \right), v_0 \right],
\]

where \( \min[^*] \) means taking a smaller value, and the constant \( C_0 \) is of the order \( v_0 \). Although Eq. (22) is derived for the directional quenching of polymer blends, we believe that it holds for DBCP as well.

When \( \delta \Psi_0/\Psi_s = 0 \) and \( f = 0.5 \), the characteristic velocity (the velocity of propagation of perturbation) \( v_0 \) is about 1/7 (lattice space/iteration), which we have determined by simulations and which is also consistent with Eq. (18). When \( \nu < v_a \) (\( v_a \) is defined in Eq. (22)), the morphology of RLM occurs, Fig. 1(b). A phase diagram on the \( \delta \Psi_0/\Psi_s = 1/\nu \) is shown in Fig. 2(b). Here the curve on the left represents Eq. (22) with \( C_0 = 1/25 \), \( C = 4/3 \), and \( v_0 = 1/7 \).

Here we should mention that the front propagation velocity of the lamellar phase (\( f = 0.5 \)) without thermal fluctuation derived by Paquette\(^\text{10}\) is written as

\[
\nu_b^0 = \left( \frac{2 \tau}{D} \right)^{1/2} \left( \tau^2 - 4\alpha D \right)^{1/2},
\]

with \( \Lambda M = 1/4 \), \( \Lambda \Lambda = 1/8 \), \( \tau = 0.35 \), and \( \alpha = 0.02 \), we obtain \( \nu_b^0 = 0.355 \equiv 1/2.82 \) (lattice space/iterations), which is much larger than the value of Eq. (18c). Our simulation results seem more consistent with the value of Eq. (18c). This discrepancy possibly originated from the nonequilibrium nature of directional quenching in our simulation.

### 3. Regular column morphology (RCM)

This is the case of very small quench boundary shifting velocity (\( \nu < v_b \)) and is corresponding to the quasistatic quenching process. In this case, the quench boundary can be regarded as a fixed boundary to some extent and domains coarsen at the quench boundary, therefore the domain morphology is determined to minimize the interfacial free-energy. When the region of the phase-separating part expands, the increment of the interfacial area is the smallest if the lamellar interface between the different phases is perpendicular to the quench boundary. It is expected that the regular column type of morphology (RCM) with \( \epsilon < 0 \), which is corresponding to the minimum of the interfacial free-energy, will occur, Fig. 1(d). This result reveals that the front propagation velocity is dependent on the orientation of the lamellae. It seems that the lamella-orientation dependence of the front propagation velocity is, at least partially, determined by the interfacial free-energy. Following the argument given by Furukawa,\(^\text{13}\) the critical velocity \( v_f \) is insensitive to the initial thermal fluctuations for the directional quenching of polymer blends. We believe that the directional quenching of DBCP shares basically the same mechanism as polymer blends. The only difference is that the column width is not only determined by the shifting velocity of the quench boundary, but also by the parameter \( \alpha \) which is inversely proportional to the square of subchain length and is related to the lamellar...
thickness $l$ through $l \sim \alpha^k$ with $\kappa = -0.256 \pm 0.003$.\textsuperscript{20} It is probably due to this reason, $\nu_i$ depends on the initial thermal fluctuation to some extent [the right-hand-side curve in Fig. 2(b)]. When the initial thermal fluctuation is absent, i.e., $\partial \Psi_i = 0$, we found $\nu_i \sim 1/25$ (lattice space/iteration). As the (initial) thermal fluctuation increases to $\partial \Psi_i = 0.1$, $\nu_i \sim 1/17$. This means that the fluctuation promotes the appearance of RCM. On the other hand, the regular perturbation from the quench boundary can not be effective if the amplitude of random fluctuation is large enough ($\partial \Psi_i / \Psi_i > 0.1$). This is quite different from the case of polymer blends where the regular perturbation from the quench boundary is still effective even when $\partial \Psi_i / \Psi_i \sim 1.0$.\textsuperscript{13}

B. Triangular phase morphologies generated by directional quenching

For the asymmetric DBCP with $f = 0.4$, the average order parameter $\Psi = 0.2$, and the equilibrium morphology is the triangular phase by homogeneous quenching. Due to the (initial) thermal fluctuation, the transient triangular phase is not very regular under the homogeneous quenching, Fig. 3. Therefore, we call it as dropletlike morphology (DLM) to distinguish it from the regular triangular morphology (RTM), Fig. 5. The selection of the unstable mode in the case of directional quenching also depends on how fast the quench boundary passes over. As the deformation factor $\epsilon$ defined in Eq. (19) is not suitable for the triangular phase, it is difficult to discuss the morphological transitions quantitatively. Instead, only the qualitative discussions are given in the following.

The domain morphologies for $f = 0.4$ and $\partial \Psi_i = 10^{-6}$ at various quench boundary shifting velocities are shown in Fig. 4. It is interesting that instead of triangular phase, the RLM (the mode of horizontal lamellae) appeared first at the intermediate quench boundary shifting velocities, $1/\nu = 15-30$, Figs. 4(a) and 4(b). As the quench boundary shifting velocity decreases further, i.e., $1/\nu > 40$, the RTM appears readily, Figs. 4(d) and 4(e). As pointed out by Paquette,\textsuperscript{10} when the system is initially perturbed, several ordered modes may be excited, but the fastest one will eventually establish itself ahead of the others. In our situation, it appears that the RLM grows faster when the quench boundary shifts moderately, Figs. 4(a) and 4(b). As the shifting velocity of the quench boundary decreases, the growing velocity of the RTM is getting faster and finally it becomes dominant, Figs. 4(c)–4(e). We should mention again that the morphologies obtained here are transient nonequilibrium morphologies. The simulation also shows that the final equilibrium morphology of Figs. 4(a) and 4(b) is RTM.

In addition to the front propagation resulting from the mismatch of the order parameters at the phase boundary between the phase-separating part and just-quenched part by the inhomogeneous quenching that produces RLM, the instability is also triggered by the thermal fluctuation perturbation. The simulation results indicated that the (initial) thermal fluctuation strongly affects the morphology, and generally promotes the emerging of RTM. One critical example is shown in Fig. 5, in contrast to the case of Fig. 4(b). The RTM is obtained when we set $1/\nu = 25$ and increase the (initial) thermal fluctuation to $\partial \Psi_i = 0.01$.

IV. SUMMARY AND REMARKS

We have presented a preliminary numerical study on the microphase separation of a two-dimensional DBCP system under directional quenching. In our numerical simulation, the microphase separation is controlled by quench boundary shifting velocity that measures the degree of irreversibility of the quenching process. We found that for the symmetric DBCP ($f = 0.5$) the lamellae orientation under directional quenching is dependent on the quench boundary shifting velocity. The irregular lamellar morphology (ILM), which is essentially equivalent to that produced by the homogeneous quenching can be obtained with fast quench boundary shifting velocity. Two regular morphologies which are the characteristics of directional quenching process are obtained at slower quench boundary shifting velocities. One of the regular lamellar morphologies has its normal of the lamellae perpendicular to the quench boundary on the average and is named as regular lamellar morphology (RLM) that is produced at initially slow quench boundary shifting velocity, whereas the other one is parallel to the quench boundary and is named as regular column morphology (RCM) that is produced at very slow quench boundary shifting velocity. The simulation reveals that the system tends to minimize the interfacial free-energy at the quench boundary when the quench boundary is shifting very slowly and it results in RCM. For the asymmetric DBCP with $f = 0.4$, which forms equilibrium morphology of triangular phase, the mode of regular lamellae morphology with the normal of lamella perpendicular to the quench boundary appears first under directional quenching when the initial thermal fluctuation is very small. By increasing the initial thermal fluctuation, the growth rate of the triangular phase gets faster. Therefore, it...
FIG. 4. The typical morphologies of triangular phase ($f=0.4$) at various shifting velocities of quench boundary with $\Delta T_c=10^{-6}$. The other model parameters are the same as that of Fig. 1(a) $1/\nu=20$; (b) $1/\nu=25$; (c) $1/\nu=30$; (d) $1/\nu=40$; (e) $1/\nu=60$. The quench boundary is shifting downwards.
FIG. 5. The regular triangular morphology (RTM) produced by directional quenching with $1/s=25$ and $\vartheta_{f_0}=0.01$. The other model parameters are the same as that of Fig. 1. The quench boundary is shifting downwards. Comparing to Fig. 4(b), it reveals that the appearance of RTM is promoted by increasing the (initial) thermal fluctuation.

seems that the thermal fluctuation promotes the emerging of the mode of regular triangular morphology in the case of $f=0.4$.

In this paper, the interface between the ordering phase and disordered phase, which we called as quench boundary, is very sharp (one lattice space). The sharp quench boundary implies that the boundary width is narrower than the wave length at the initial instability created by a homogeneous quenching, $\lambda_{\text{in}}$, defined in Eq. (14). There are some technical difficulties to generate such narrow quench boundary. On the other hand, the regular morphologies will be more difficult to emerge as the quench boundary becomes broader. However, as already pointed out by Furukawa, the mathematically narrow quench boundary does not necessarily correspond to the physically narrow quench boundary. Due to the existence of the time lag for the quenched phase to start to order, there is a preordering region between ordering and disordered region. Therefore, the application of a sharp quench boundary still provides an effective quench boundary with finite boundary width.

Although, for simplicity, we have only considered the microphase separation in two-dimensional DBCP systems induced by directional quenching, the qualitative conclusions obtained for the two-dimensional system will also hold for the three-dimensional system as has been demonstrated for polymer blends by Furukawa. As a matter of fact, very thin films of DBCP, which can be considered as two-dimensional systems, have their special technological importance. For example, recently, a styrene–butadiene DBCP thin film has been used as templates for nanolithography on a large scale which is not accessible by other techniques. Therefore, we should mention here that the present study is significant from not only the fundamental polymer physics but also the technology from which to make macroscopically ordered DBCP materials efficiently. Therefore, this topic deserves more detailed theoretical and experimental study.

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1For example, M. Cross, and P. Hohenberg, Rev. Mod. Phys. 65, 851 (1993).