

Dynamic Density Functional Approach for Diblock Copolymer Films in the Presence of an Electric Field

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We investigate mesophase separations of diblock copolymer films subjected to an electric field in the framework of dynamic density functional theory. The lamellae are taken to be ordered parallel to the confining surfaces in weak electric fields. Strong enough electric fields globally orient the lamellae in the direction parallel to the electric field. We observe selective disordering for strong electric fields. In certain intermediate electric fields, the ordering dynamics is a superposition of parallel and perpendicular lamellar formation. We construct the phase diagram as a function of the electric field strength and the film thickness. Our results are in good agreement with the prediction of the strong-segregation theory.

Key words: diblock copolymer, electric field, wetting, dynamic density functional theory, strong-segregation theory

1. INTRODUCTION

Block copolymers offer a wealth of self-assembling, ordered nanoscopic morphologies that have tremendous potential as lithographic templates, high-density porous media, and scaffolds for nanoscopic devices. In practice, however, systems quenched into ordered phase regions often consist of poorly aligned lamellae or domains of lamella which are aligned in different directions. This situation is not satisfactory in industrial points of view. Since the thermodynamic driving force for alignment is weak, external fields such as mechanical shears and interfacial interactions have been used to drive alignment. This technique is very useful for bulk systems, but it cannot be applied easily to thin films due to their thickness. Recently, alignment of block copolymer micro-structure by electric fields has been studied [1-5,11-14]. Morkved *et al.* showed that electric fields are ideally suited to the local control of the domain orientation in block copolymer thin films [1].

In previous theoretical works on this topic, Onuki and Fukuda have investigated the dynamics of undulation in two-dimensional lamellar systems both numerically and analytically [11,12]. Amundson *et al.* have considered possible mechanisms of lamellar alignment by a theoretical analysis of electric field-induced forces on different types of defects in microstructures [4]. Very recently Tsori and Andelman investigated the alignment of thin film diblock copolymers subject to a perpendicular electric field in both weak and strong segregation regimes [13]. We study a more general case of dynamics of mesophase formation in the framework of dynamic density functional theory (DDFT) for a diblock copolymer melt. Fraaije *et al.* are currently investigating the same application [14].

In diblock copolymer films confined between two electrodes, there is a competition between two fields, surface field and electric field, which favor alignment of the lamella parallel to and perpendicular to the surfaces, respectively. In this paper, we demonstrate how

orientation due to the electric field and that due to the surface field compete in lamellar phases. We also investigate the influence of confinement and electric field on the stabilization of lamellar morphology. We construct the phase diagram as a function of the strength of electric field and the film thickness. We compare our calculations with the results calculated using strong-segregation theory (SST) [5,10,13]. Phase diagram calculated using DDFT agrees well with the description of strong-segregation theory.

2. MODEL AND TECHNIQUES

We consider a system of n diblock copolymer Gaussian chains of the length $N = N_A + N_B$ confined between two flat surfaces in a volume $V = H \times \Delta_0 \times \Delta_0$. H denotes the film thickness, Δ_0 is the lateral extension of the film. There is a short range repulsion between the two monomer species which can be parameterized by the Flory-Huggins parameter χ_{AB} , which is set to $\chi_{AB} = 1$. Both confining surfaces are parallel, impenetrable and attract the A-component of the diblock and repel the B-component via a short range interaction. The differences in A-surface and B-surface energies can be parameterized by the Flory-Huggins parameter differences $\Delta\chi_S \equiv \chi_{BS} - \chi_{AS}$. The surface interaction parameter is set to $\Delta\chi_S = 1$ or $\Delta\chi_S = 0.1$. Periodic boundary conditions are imposed in the x and y directions. An electric field is imposed in the z direction. The model we used here is based on the dynamic mean-field density functional theory proposed by Fraaije for the microphase separation dynamics of block copolymers [6]. We extend the dynamic density functional method to polymer liquids under an electric field. In contrast to phenomenological theories (Cahn-Hilliard, Oono-Puri, and Flory-Huggins-de Gennes), it retains the full polymer path integral by a numerical procedure. The benefit of such an approach is that it allows for the description of the mesoscopic dynamics of a specific complex polymer liquid.

In the dynamic density functional theory, the free energy functional $F[\Psi_i]$ for copolymer melts is given by

$$F[\Psi_i] = -k_B T \ln \frac{Z^n}{n!} - \sum_i \int_{\bar{r}} U_i(\bar{r}) \Psi_i(\bar{r}) d\bar{r} + \frac{k_B T}{2} \sum_{i,j} \chi_{ij} \int_{\bar{r}} \eta(\bar{r} - \bar{r}') \Psi_i(\bar{r}) \Psi_j(\bar{r}') d\bar{r} d\bar{r}' - \frac{1}{2} \int \varepsilon(\bar{r}) |\bar{E}(\bar{r})|^2 d\bar{r} \quad (1)$$

where Ψ_i is the volume fraction of i -type segments, i is the index of each component (A or B), n is the number of polymer molecules, Z is the single-chain partition function. The external potential U_i is conjugate to the volume fraction Ψ_i via the Gaussian chain density functional [6]. The third term expresses the cohesive interactions energy. The χ_{ij} is the Flory-Huggins interaction parameter (so-called χ parameter) and $\eta(\bar{r} - \bar{r}')$ is the short-range interaction function, which is replaced by a summation over nearest neighbors ($\eta \propto \delta(\bar{r} - \bar{r}')$). The summation over i, j is performed over all the segment types in the system, including the wall surface S [7]. The last term represents the electrostatic contribution to the free energy.

For conserved order parameters, the time-dependent Ginzburg-Landau (TDGL) model of phase separation of a polymer blend or a block copolymer melt is given by the equation

$$\frac{\partial \Psi_i}{\partial t} = M_i \nabla \cdot (\Psi_i \nabla \mu_i), \quad (2)$$

where $\mu_i \equiv \delta F / \delta \Psi_i$ is the chemical potential, M_i is the mobility coefficient, which is assumed to be a constant. As a minimal model, we ignore any hydrodynamic effects and possible non-locality in the mobility coefficient. We will also ignore the noise term in subsequent discussions except to include it as providing an initial randomness in the system.

We introduce $G_i(\bar{r}, s; \bar{r}')$ which represents the statistical weight (or the partition function) of the i -type chain which starts from \bar{r}' and \bar{r} at in s steps. $G_i(\bar{r}, s; \bar{r}')$ satisfies the modified diffusion equation,

$$\frac{\partial G_i(\bar{r}, s; \bar{r}')}{\partial s} = \left[\frac{a^2}{6} \nabla^2 - \beta U_i(\bar{r}) \right] G_i(\bar{r}, s; \bar{r}'), \quad (3)$$

and the initial condition

$$G_i(\bar{r}, 0; \bar{r}') = \delta(\bar{r} - \bar{r}'). \quad (4)$$

For diblock copolymers, the volume fraction can be calculated from the Green's functions as

$$\Psi_A(\bar{r}) = \frac{n}{Z} \int_0^{N_A} ds \int_{\bar{r}_A} d\bar{r}_A d\bar{r}_j d\bar{r}_B \times G_A(\bar{r}_A, N_A - s; \bar{r}) G_A(\bar{r}_A, s; \bar{r}_j) G_B(\bar{r}_j, N_B; \bar{r}_B). \quad (5)$$

We assume that the local dielectric permittivity $\varepsilon(\bar{r})$ is composed of a linear combination of the dielectric permittivities ε_i of the various pure components:

$$\varepsilon(\bar{r}) = \sum_i \varepsilon_i \Psi_i(\bar{r}). \quad (6)$$

The electric field strength $\bar{E}(\bar{r})$ can be determined by solving the Maxwell equation for the case where there are no free charges:

$$\nabla \cdot (\varepsilon(\bar{r}) \bar{E}(\bar{r})) = 0 \quad (7)$$

The mean-field intrinsic chemical potentials can easily be derived by functional derivatives of the free energy:

$$\mu_i(\bar{r}) = -U_i(\bar{r}) + k_B T \sum_j \chi_{ij} \int_{\bar{r}'} \eta(\bar{r} - \bar{r}') \Psi_j(\bar{r}') d\bar{r}' - \frac{1}{2} \varepsilon_i |\bar{E}(\bar{r})|^2. \quad (8)$$

In our simulations, we used the dimensionless electric field that is defined by

$$\bar{E}_0(\bar{r}) \equiv \left[\frac{\varepsilon_0 d^3}{k_B T} \right]^{1/2} \bar{E}(\bar{r}), \quad (9)$$

where d is the mesh size and ε_0 is the vacuum permittivity. The dielectric permittivities are taken to be $\varepsilon_A = 4\varepsilon_0$ and $\varepsilon_B = 2\varepsilon_0$.

3. RESULTS AND DISCUSSION

First we investigate how microphase separation of symmetric diblock copolymers proceeds in the presence of electric field and surface field. There is a competition between two fields, surface field and electric field, which favor alignment of the lamella parallel to and perpendicular to the surfaces, respectively. In other words, surface interactions stabilize stacking of lamellae in a direction parallel to the surface, whereas an electric field has an anisotropic destabilizing effect on lamellar microstructure.

Figure 1 shows the pattern evolution of phase separation in a weak electric field for strong surface field $\Delta\chi_S = 1$. Even at an early time, $t = 20$, a damped oscillatory behavior can be observed. Thus the system starts to line up with the wall at a very early time. We find that the density profile near the surface does not change appreciably at late times, indicating that several layers nearest the confining surface have reached their equilibrium value. On the other hand, in a region halfway between electrodes, the oscillation is yet to attain the equilibrium value at a very early time. In Fig. 1b and 1c, we can observe the frustration release process.

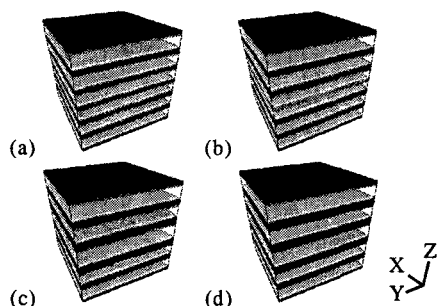


FIG. 1. Lamellar formation of an A_8B_8 copolymer melt at dimensionless times (a) $t=20$, (b) $t=40$, (c) $t=60$, and (d) $t=100$ in the presence of the weak electric field, $E_0 = 0.1$.

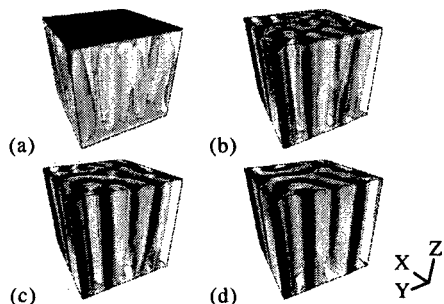


FIG. 2. Lamellar formation of an A_8B_8 copolymer melt at (a) $t=20$, (b) $t=40$, (c) $t=60$, and (d) $t=100$ in the presence of the strong electric field, $E_0 = 2.0$.

Frustration in a parallel lamellar phase can be relieved if the parallel lamellae flip forming lamellae with the bulk lamellar period. The final morphology for weak electric fields is the parallel lamellar phase without any defects.

Figure 2 shows the same as in Fig. 1 but for the strong electric field $E_0 = 2.0$. In contrast to the weak electric field case, here the surface-induced ordering is suppressed by the electric field. Phase separation proceeds in the plane perpendicular to the electric field. We find that strong enough electric fields globally orient the lamellae in the direction parallel to the electric field, whereas there are some defects in the plane perpendicular to the electric field. The final morphology is a partially wet perpendicular lamellar phase. The 3D defect structure in Fig. 2d is remarkably similar to the sketch in Ref. 4, based on experimental results for poly(styrene-block-methyl methacrylate) melt in an electric field.

Figure 3 presents the lamellar formation similar to the one in Fig. 1 except now the electric field strength is set to $E_0 = 0.5$. In certain intermediate E fields, the dynamics is a superposition of parallel and perpendicular lamellar formation. At a very early time, one can observe surface-induced ordering as in Fig. 1. We find that electrostatic effect becomes important only in the later stages of phase separation (see Fig. 3b). The process of reorientation from parallel to perpendicular lamellae is demonstrated. Different structural changes such as undulation of lamellae, breakup, and recombination can be clearly observed (see Fig. 3). The process consists of defect formation and breakup, which is followed by recombination of pieces of lamellae from neighboring layers. Thus, the mixed lamellar phase is formed. Figure 4 shows the final morphology of AB block copolymer melts for an intermediate electric field

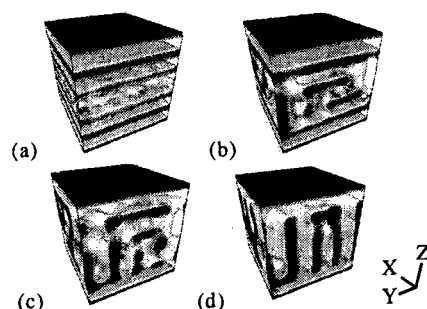


FIG. 3. Lamellar formation of an A_8B_8 copolymer melt at (a) $t=20$, (b) $t=60$, (c) $t=100$, and (d) $t=150$ in the intermediate electric field, $E_0 = 0.5$.

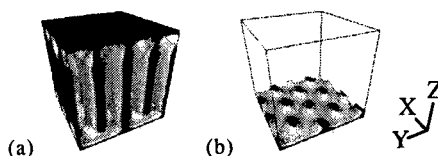


FIG. 4. Mixed lamellar structure of an A_8B_8 copolymer melt for $E_0 = 0.5$: (a) Morphology of A beads at (b) $t=1000$, (b) view of a region near the confining surface, indicating the "hexagonally wet" mixed lamellar phase.

$E_0 = 0.5$. In Fig. 4a, we can easily see the mixed lamellar morphology where the parallel monolayer forms adjacent to the confining surfaces, while the interior region has perpendicular layers. To view a region near the surface more precisely, in Fig. 4b, we show the same structure shown in Fig. 4a. The "hexagonally wet" mixed lamellar phase is observed. The stability of this structure crucially depends on surface field strength and electric field strength. As can be seen from Fig. 1, for small electric fields, the lamellae are in the fully parallel configuration. When the applied electric field is large enough to destroy the parallel layer nearest the confining surface, the lamellae are in a perpendicular lamellar configuration (see Fig. 2). In the intermediate electric field, the mixed lamellar structure is formed (see Fig. 4).

Finally, we consider the phase diagram for this system. At high incompatibility ($\chi N \gg 10.5$), many features of confined diblock copolymers can be reduced from the strong segregation theory. This has been applied to study the effect of confinement by Turner [7] and Walton *et al* [8]. Pereira and Williams extend the strong segregation theory to diblock copolymer films under an electric field [5]. In strong segregation regime, the lamellae are not easily deformed, and the effect of the surface field is important only close to the confining wall.

Figure 5 shows the phase diagram for intermediately segregated ($\chi N = 16$) symmetric diblock films confined between two identical surfaces. Results are calculated both DDFT and SST for weak surface fields. The surface interaction parameter is set to $\Delta\chi_s = 0.1$ in DDFT. In weak electric fields, the parallel lamellar (L_v^{\parallel}) phase is stable due to the effect of wetting. The index v denotes the number of A/B interfaces parallel to the film. In large electric fields, the perpendicular lamellar phase (L^{\perp}) is stable due to the effect of the electric field. For

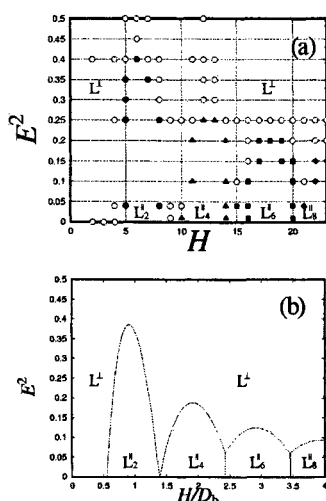


FIG 5. Phase diagrams for symmetric diblock copolymer films confined between identical walls calculated using (a) dynamic density functional theory and (b) strong-segregation theory. The lamellar phases are labeled as L^1 (parallel lamellar), L^1 (perpendicular lamellar). In (a), the symbols refer to various morphologies: open circle L^1 , solid circle L^2 , solid triangle L^3 , solid square L^4 , and solid diamond L^5 . Diagrams are plotted in terms of (a) the film thickness H vs electric field squared E^2 and (b) the film thickness H relative to the bulk lamellar period D_b vs electric field squared E^2 .

ultra thin films, i.e., less than a monolayer, a perpendicular lamellar phase (L^1) is favored because this is the only way the lamellae can be close to their preferred spacing. As the film gets thicker, a parallel phase (L^2) is observed. The critical electric field is found above which a perpendicular lamellar phase is preferred over a parallel lamellar phase. This critical electric field decreases with typical oscillations of period D_b as the film thickness H increases. These oscillations are caused by the frustration occurring when the film thickness H is incommensurate with the bulk lamellar period D_b . The phase diagram in E - H plane using DDFT is in good agreement with the description of the strong-segregation theory.

4. CONCLUSIONS

We have studied the influence of an electric field, surface field, and confinement on the morphology of diblock copolymers in the framework of dynamic density-functional theory. We have demonstrated how lamellar formation proceeds in the presence of electric field and surface field. The lamellae are taken to be ordered parallel to the confining surfaces in weak electric fields. Frustration in a parallel lamellar phase can be relieved if the parallel lamellae flip forming lamellae with the preferred lamellar period D_b . Strong enough electric fields globally orient the lamellae in the direction parallel to the electric field line, whereas there are some defects in the plane perpendicular to the electric field. In strong electric fields, we demonstrate that the formation of boundaries along the z direction is

suppressed by the electric field. This effect is called the selective disordering which is in agreement with earlier predictions [4]. In certain intermediate electric fields, the ordering dynamics is a superposition of parallel and perpendicular lamellar formation. The reorientation process from parallel to perpendicular lamellae is demonstrated. The "hexagonally wet" mixed lamellar phase is observed for certain electric fields.

We have constructed the phase diagram as a function of electric field strength and the film thickness. When the surface field is weak (namely $\Delta\chi_s$ is small), the first-order phase transition to the perpendicular state occurs when the electric field is increased above the threshold electric field. We find that this critical electric field decreases with typical oscillations of period D_b as the film thickness H increases. This is considered to be due to the effect of lamellae frustration. Our results agree well with the prediction of the strong segregation theory developed by Pereira and Williams [5], Ashok *et al.* [10], Tsori and Andelman [13].

We have concentrated here on the lamellar phase of a diblock melt. However, our method is also applicable to other phases, such as hexagonal cylinders, bcc spheres and gyroid morphology. Such a trial is now under way.

5. ACKNOWLEDGEMENT

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