

Surface induced ordering in thin film diblock copolymers: Tilted lamellar phases

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We investigate the effect of chemically patterned surfaces on the morphology of diblock copolymers below the order–disorder transition. Profiles for lamellar phases in contact with one surface, or confined between two surfaces are obtained in the weak segregation limit using a Ginzburg–Landau expansion of the free energy, and treating it with mean-field theory. The periodically patterned surface induces a tilt of the lamellae in order to match the surface periodicity. The lamellae relax from the constrained periodicity close to the surface to the bulk periodicity far from it. The phases we investigate are a generalization to the mixed (perpendicular and parallel to the surface) lamellar phases occurring when the two surfaces are homogeneous. A special case when the surface pattern has a period equal to the bulk lamellar period showing “T-junction” morphology is examined. Our analytic calculation agrees with previous computer simulations and self-consistent field theories.
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I. INTRODUCTION

Diblock copolymers are made up of two chemically distinct polymer chains which are covalently bonded together. The process of macroscopic phase separation usually occurring for incompatible chains is suppressed because of the imposed connectivity between the two blocks. Instead, the system may undergo a mesoscopic phase separation. The thermodynamic state of the system depends on two parameters:^{1–5} the fraction of the A monomers $f = N_A/N$ and χN , where N_A and N_B are the lengths of the A- and B-block, respectively, and N is the polymerization index, $N = N_A + N_B$. The Flory parameter χ measures the interaction energy (in units of $k_B T$, the thermal energy) between two monomers and is positive if the two monomers repel each other. For symmetric melt ($f = \frac{1}{2}$) and small χ (high temperature), the disordered, homogeneous phase has the lowest free energy. Increasing χ above the order disorder transition (ODT) point, $\chi = \chi_c$ (lowering the temperature), results in a phase transition to a lamellar phase. For a fixed $\chi > \chi_c$, and as a function of the A/B asymmetry ($f \neq \frac{1}{2}$) the prevailing mesoscopic ordered phases can have hexagonal or cubic symmetries as well.^{3,4}

When a block copolymer (BCP) melt is put in contact with a surface, the surface reduces the chain entropy. In addition, it interacts chemically with the blocks, leading to a surface behavior which can be very different from that of the bulk. Fredrickson⁶ has considered BCP in contact with a uniform surface having preferred interaction to one of the blocks. In the weak-segregation regime, he used mean-field theory to investigate systems both below and above the ODT. Above, but close to the ODT, the order parameter (being the deviation of the A monomer concentration from its average

value f) has decaying oscillations characterized by a correlation length ξ . Approaching the ODT, ξ diverges, and below the ODT the system is characterized by a spatially modulated order parameter.⁶

The situation is more complex for a copolymer melt confined between two surfaces. For a thin-film of BCP melt, the interplay of the spacing $2L$ between the surfaces, the Flory parameter χ , and the surface interactions results in a rich interfacial behavior.^{7,8} The phase behavior of thin BCP films subject to uniform surface fields has been investigated numerically using self-consistent field (SCF) theory^{9,10} and Monte-Carlo simulations,^{7,11} and was found to consist of parallel, perpendicular and mixed lamellae denoted L_{\parallel} , L_{\perp} , and L_M , respectively. The latter L_M phase has parallel lamellae extending from one surface, which are jointed in a T-junction defect with perpendicular lamellae extending from the opposite surface.^{12,13} At a given inter-surface spacing, increasing the (uniform) surface interactions promotes a parallel orientation with either A-type or B-type monomers adsorbed to the surface. However, if the spacing $2L$ between the surfaces is incommensurate with the lamellar periodicity, or the incompatibility χ is increased, a perpendicular orientation is favored.¹⁴

In the present paper we analytically derive expressions for the order parameter of a BCP melt confined between two parallel flat surfaces, below the bulk ODT temperature, and in the weak-segregation limit. In Sec. II we introduce a model of a confined BCP melt in contact with either homogeneous or sinusoidally patterned surfaces.¹⁵ Contrary to the system above the ODT, studied earlier in a separate work,^{8,16} a linear response theory assuming small order parameter as a response to the surface fields is inadequate, since the bulk phase has an inherent spatially varying structure. Instead, in Sec. III an expansion is carried out around a tilted lamellar phase of the bulk. A simple ansatz for the deviation of the

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order parameter from its bulk value is suggested, utilizing the symmetry of the problem. A close similarity is shown between this problem and the symmetric tilt grain boundaries, with a mathematical solution very similar to what has been derived in Ref. 17. In Sec. IV the problem of one patterned surface is extended to a melt confined between two surfaces, one being chemically patterned while the second is chemically homogeneous. We obtain confined tilted lamellar phases, and, in particular, L_M phases. The lamellae extending from the patterned surface merge with the parallel ordering induced by the homogeneous surface.

II. THE MODEL

When a BCP system in the disordered (high temperature) phase is cooled below the ODT, a lamellar phase forms^{18,19} for $f = \frac{1}{2}$ (symmetric) or when $|f - \frac{1}{2}|$ is small. The behavior of such systems was modeled numerous times in the past^{4,8,16,20-22} using coarse grained Ginzburg-Landau free energy. A possible form (in units of $k_B T$) used throughout this paper is

$$\mathcal{F}_b = \int \left\{ \frac{1}{2} \tau \phi^2 + \frac{1}{2} h [(\nabla^2 + q_0^2) \phi]^2 + \frac{u}{4!} \phi^4 - \mu \phi \right\} d^3 \mathbf{r}, \quad (1)$$

where

$$q_0 \approx 1.95/R_g, \quad (2)$$

$$\tau = 2\rho N(\chi_c - \chi), \quad (3)$$

$$\chi_c \approx 10.49/N, \quad (4)$$

$$h = 3\rho c^2 R_g^2 / 2q_0^2. \quad (5)$$

The copolymer order parameter ϕ is defined as $\phi(\mathbf{r}) \equiv \phi_A(\mathbf{r}) - f$, the deviation of the local A monomer concentration from its average value. R_g is the gyration radius of the chains ($R_g^2 \approx \frac{1}{6} N a^2$ for Gaussian chains) and the chain density ρ is equal to $1/N a^3$ for an incompressible melt. The chemical potential is μ while u/ρ and c are dimensionless parameters of order unity. Hereafter we set the monomer size to unity, $a = 1$, expressing all lengths in units of a . By choosing $u/\rho = c = 1$ (and recalling that $f = \frac{1}{2}$), all parameters in the model are given in terms of χ and N .

Above the ODT, $\chi < \chi_c$, the free energy (1) describes a system in the homogeneous, disordered phase having a uniform order parameter $\phi = 0$. This system has been previously studied by us in Ref. 16. Below the ODT, $\chi > \chi_c$, the lamellar phase of period $d_0 = 2\pi/q_0$ becomes stable. Close to the ODT, $\chi \approx \chi_c$, (weak segregation limit), the order parameter is given in the single q -mode approximation as $\phi(\mathbf{r}) = \phi_0 + \phi_q \cos(\mathbf{q}_0 \cdot \mathbf{r})$, and for symmetric BCP ($f = \frac{1}{2}$), used throughout the paper, $\langle \phi(\mathbf{r}) \rangle = \phi_0 = 0$. It is worthwhile to mention that similar free energy functionals have been used to describe bulk and surface phenomena in diblock copolymers,^{3,4,17,18} amphiphilic systems,²³ Langmuir films,²⁴ and magnetic (garnet) films.²⁵

The interaction of the BCP with the confining surfaces is assumed to be short-range and limited to the surface only. The surface free energy \mathcal{F}_s (in units of $k_B T$) has the form:

$$\mathcal{F}_s = \int \left\{ \sigma(\mathbf{r}_s) \phi(\mathbf{r}_s) + \tau_s \phi^2(\mathbf{r}_s) \right\} d^2 \mathbf{r}_s, \quad (6)$$

where the integration is carried out over all surface positions $\{\mathbf{r}_s\}$. At a point \mathbf{r}_s on the surface, the first term is proportional to the order parameter, with $\sigma(\mathbf{r}_s)$ being a surface field. The magnitude $\sigma(\mathbf{r}_s)$ of this surface field can be controlled by coating the substrate with random copolymers.^{26,27} The second (quadratic) term allows us to describe cases where the local surface segregation is different than the bulk: a positive τ_s means local increase of the Flory parameter χ and a lower phase transition temperature.

The surface effects are contained in the correction to the order parameter

$$\delta\phi(\mathbf{r}) \equiv \phi(\mathbf{r}) - \phi_b(\mathbf{r}), \quad (7)$$

where the bulk order parameter $\phi_b(\mathbf{r})$ in the symmetric lamellar phase is given by

$$\phi_b(\mathbf{r}) = \phi_q \cos(\mathbf{q}_0 \cdot \mathbf{r}), \quad (8)$$

$$\phi_q^2 = -8\tau/u. \quad (9)$$

The bulk ϕ_b does not depend on surface properties, and recall that $\tau < 0$ below the ODT. The total free energy $\mathcal{F} = \mathcal{F}_b + \mathcal{F}_s$ is now expanded about its bulk value $\mathcal{F}[\phi_b]$ to second order in $\delta\phi$: $\mathcal{F} = \mathcal{F}[\phi_b] + \Delta\mathcal{F}$, with

$$\begin{aligned} \Delta\mathcal{F} = & \int \left\{ [(\tau + hq_0^4) \phi_b + \frac{1}{6} u \phi_b^3 + hq_0^2 \nabla^2 \phi_b - \mu] \delta\phi \right. \\ & + \frac{1}{2} (\tau + \frac{1}{2} u \phi_b^2) (\delta\phi)^2 + \frac{1}{2} h [(\nabla^2 + q_0^2) \delta\phi]^2 \left. \right\} d^3 \mathbf{r} \\ & + \int \left\{ \sigma(\mathbf{r}_s) \delta\phi(\mathbf{r}_s) + 2\tau_s \phi_b(\mathbf{r}_s) \delta\phi(\mathbf{r}_s) \right. \\ & \left. + \tau_s \delta\phi^2(\mathbf{r}_s) \right\} d^2 \mathbf{r}_s. \end{aligned} \quad (10)$$

This expansion is valid in the weak segregation limit and for small enough surface fields. In the next section we find the function $\delta\phi(x, y, z)$ that minimizes the free energy functional $\Delta\mathcal{F}$ for a given choice of bulk morphology $\phi_b(\mathbf{r})$ and surface field $\sigma(\mathbf{r}_s)$.

III. BCP MELT CONFINED BY ONE PATTERNED SURFACE

When the confining substrate is spatially modulated, at least one additional length scale enters the problem. Numerical studies of thin BCP film below the ODT temperature in the presence of sinusoidally patterned surfaces of period d_x have been carried out by Petera and Muthukumar.²⁸ It was found that the lamellae are tilted with an angle $\theta \equiv \arccos(d_0/d_x)$ with respect to the normal to the surface. We proceed along similar lines, assuming that the pattern located at $y = 0$ [see Fig. 1(a)] is described by a single harmonic,

$$\sigma(x, z) = \sigma(x) = \sigma_0 + \sigma_q \cos(q_x x) \quad (11)$$

and is translational invariant in the z -direction. The parameter σ_q sets the strength of the modulation mode, while the average $\langle \sigma(x) \rangle$ is given by σ_0 . Throughout this section we assume $\sigma_0 = 0$, hence the surface is overall neutral to the A/B

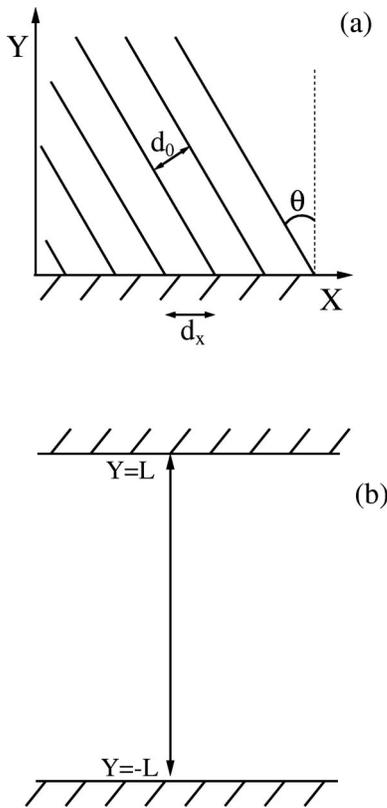


FIG. 1. Schematic drawing of the BCP film. In (a) the BCP melt of periodicity d_0 is confined by a flat patterned surface at $y=0$. The tilt angle with the normal to the surface is θ , (see Sec. III). In (b) the melt is confined by a patterned surface at $y=-L$ and a homogeneous surface at $y=L$ (Sec. IV).

adsorption. Furthermore, the periodicity $d_x=2\pi/q_x$ along the x -axis is assumed to be longer than the natural lamellar periodicity d_0 in the bulk, $d_x>d_0$.

The surface field $\delta\phi$ is the response of the BCP system to the presence of the surface field σ . It is expected to vanish far away from the surface:

$$\lim_{y \rightarrow \infty} \delta\phi(x, y, z) = 0 \quad (12)$$

recovering the bulk $\phi = \phi_b$ phase. In general, the bulk lamellae can be tilted with respect to the $y=0$ surface:

$$\phi_b(x, y) = \phi_q \cos(q_0 \cos \theta x + q_0 \sin \theta y + \alpha) \quad (13)$$

and this form of ϕ_b will be used as a zeroth order approximation to $\phi(x, y)$. Note that the bulk free energy Eq. (1) is invariant with respect to rotations and translations of the lamellae, and does not depend on the tilt angle θ and the phase shift α . These parameters are chosen such that they minimize the surface free energy Eq. (6). The tilt angle θ determines the overlap of the lamellae with the surface inhomogeneities, while the phase shift α distinguishes between two identical tilts, in-phase ($\alpha=0$) and out-of-phase ($\alpha=\pi$) with respect to the surface. Upon integrating the x variable, the surface free energy Eq. (6) is minimized if the angle θ obeys $\cos \theta = q_x/q_0$ and $\alpha = \pi$. Therefore, we use below a bulk phase ϕ_b given by

$$\phi_b = -\phi_q \cos(q_x x + q_y y), \quad (14)$$

$$q_x = q_0 \cos \theta, \quad q_y = q_0 \sin \theta. \quad (15)$$

For the correction order parameter $\delta\phi$ we choose

$$\delta\phi(x, y) = g(y) \cos(q_x x). \quad (16)$$

This correction describes a lamellar ordering perpendicular to the surface, and commensurate with its periodicity $d_x = 2\pi/q_x$. The overall morphology of the lamellae is a superposition of the correction field $\delta\phi$ with the bulk tilted phase, having a periodicity d_0 . The region where the commensurate correction field $\delta\phi$ is important is dictated by the amplitude and range of the amplitude function $g(y)$. It is now possible to use ansatz (16) to integrate out the x dependence in the free energy, Eq. (10), resulting in an effective one-dimensional free energy¹⁷

$$\begin{aligned} \Delta F(y) = & -\frac{1}{2} \tau \cos^2(q_y y) g^2 + \frac{1}{4} h (q_y^2 g + g'')^2 \\ & + \frac{1}{2} [\sigma q g + \tau_s (g^2 - 2\phi_q g)] \delta(y). \end{aligned} \quad (17)$$

For convenience we have included the surface free energy terms of Eq. (6) by the use of a Dirac delta function $\delta(y)$.

Applying the variational principle with respect to $g(y)$ yields a master equation:

$$[A + C \cos(2q_y y)] g(y) + B g''(y) + g''''(y) = 0, \quad (18)$$

with parameters A , B and C given by

$$\begin{aligned} A &= -\tau/h + q_y^4, \\ B &= 2q_y^2, \\ C &= -\tau/h. \end{aligned} \quad (19)$$

The equation is linear in $g(y)$ since the free energy is expanded to second order around its bulk solution ϕ_b . Clearly the bulk solution ($g \equiv 0$) solves the Euler–Lagrange equation, and hence Eq. (18) is homogeneous. The boundary conditions on the $y=0$ surface are

$$\begin{aligned} \sigma_q - 2\tau_s \phi_q + 2\tau_s g(0) + h q_y^2 g'(0) + h g'''(0) &= 0, \\ q_y^2 g(0) + g''(0) &= 0. \end{aligned} \quad (20)$$

Hence the fourth order differential equation (18) has to satisfy two boundary conditions, mixing the value $g(0)$ and its first three derivatives at the surface.

Consider the Euler–Lagrange equation (18) obeyed by the function $g(y)$. It is similar to the Schrödinger equation for an electron in a periodic one-dimensional potential $V(y) = -C \cos(2q_y y)$, the “kinetic energy” term being proportional to B , and the electron “total energy” A . Note that unlike the quantum mechanical problem, here we have, in addition, a fourth order derivative term g'''' . Moreover, the coefficient B depends on the periodicity of the potential. Nevertheless, the general form of $g(y)$ can be written, similar to the quantum mechanical problem, in terms of the Bloch form:

$$g(y) = e^{-ky} \sum_n a_n e^{2in q_y y} + \text{c.c.} \quad (21)$$

The surface induced deformations of lamellar phases are similar to the deformations appearing in the symmetric tilt grain boundaries.²⁹ The plane of symmetry between adjacent

grains corresponds to the solid confining surface of our system, and in both cases packing frustration near the interface plays an important role. However, the fact that the surface can have (nonuniform) interactions with the copolymer melt results in a richer set of phenomena in the system studied here.

We now briefly mention how Eq. (18) can be solved. More details can be found in Refs. 17 and 30. The form (21) is substituted in Eq. (18) yielding a recurrence relation between the coefficients $\{a_n\}$. Only for a special value of the eigenvalue (wavenumber) k , the series in Eq. (21) converges. Once k is determined iteratively, the full solution of Eq. (18) is given analytically by Eq. (21). If k is a solution, then so are $-k$, k^* and $-k^*$, recalling that Eq. (18) is a fourth-order differential equation. The periodicity of the “potential term” is determined by q_y , which depends on the surface periodicity $d_x = (2\pi/q_y)\tan\theta$. Modification of d_x smoothly changes $\text{Im}(k)$ until it becomes equal to an integer multiple of q_y . At these degenerate values of d_x , the plot of $\text{Re}(k)$ as a function of d_x has two branches, each branch corresponding to one possible solution of k . The values of d_x where the degeneracy appears are determined by the proximity to the ODT. For a semi-infinite BCP bounded by a single surface, the function $g(y)$ vanishes at infinity, allowing the use of only those k eigenvalues whose real part is positive, $g \sim \exp[-\text{Re}(k)y] \rightarrow 0$ as $y \rightarrow \infty$.

In Fig. 2 we examine the BCP melt confined by one sinusoidally patterned surface, $\sigma(x) = \sigma_q \cos(q_x x)$, with no preference on average to one of the blocks, $\langle \sigma \rangle = 0$, for several values of surface period $d_x = 2\pi/q_x$, and for the fixed value of the Flory parameter $\chi > \chi_c$. The main effect of increasing the surface period d_x with respect to d_0 is to stabilize tilted lamellae with increasing tilt angle. Note that even for $d_x = d_0$ [Fig. 2(a)] yielding no tilt, the perpendicular lamellae have a different structure close to the surface as is induced by the surface pattern.

Although the surface interactions are assumed to be strictly local, the connectivity of the chains causes surface-bound distortions to propagate into the bulk of the BCP melt. Using the analogy with the grain boundary problem,¹⁷ we conclude that the width D of the deformation close to the surface has a $D \sim 1/\theta$ scaling for small θ , which means that $D \sim (1 - d_0/d_x)^{-1/2}$. However, in a thin film system as is realized in experiments, this width may be too large to be detected if D is larger than the inter-surface separation $2L$.

The copolymer deformations are particularly important close to the ODT ($\chi \gtrsim \chi_c$), where deviations from the optimal lamellar shape do not cost much energy (in contrast to the strong segregation case $\chi \gg \chi_c$), and the melt can adjust more easily to the surface pattern. In Fig. 3 we show the same series of plots as in Fig. 2, but with the value of the Flory parameter $N\chi = 10.6$, closer to its critical value, $N\chi_c \approx 10.49$. The perfect lamellar shape is more distorted.

Concentration variations are governed by the profile function $g(y)$, and increase as σ_q increases. In Fig. 4 the Flory parameter χ and the repeat period d_x are held fixed, while the correction $\delta\phi$ increases as σ_q is increased from 1 in (a), to 2 in (b), to 4 in (c), in units of $hq_0^3\phi_q$. Strong

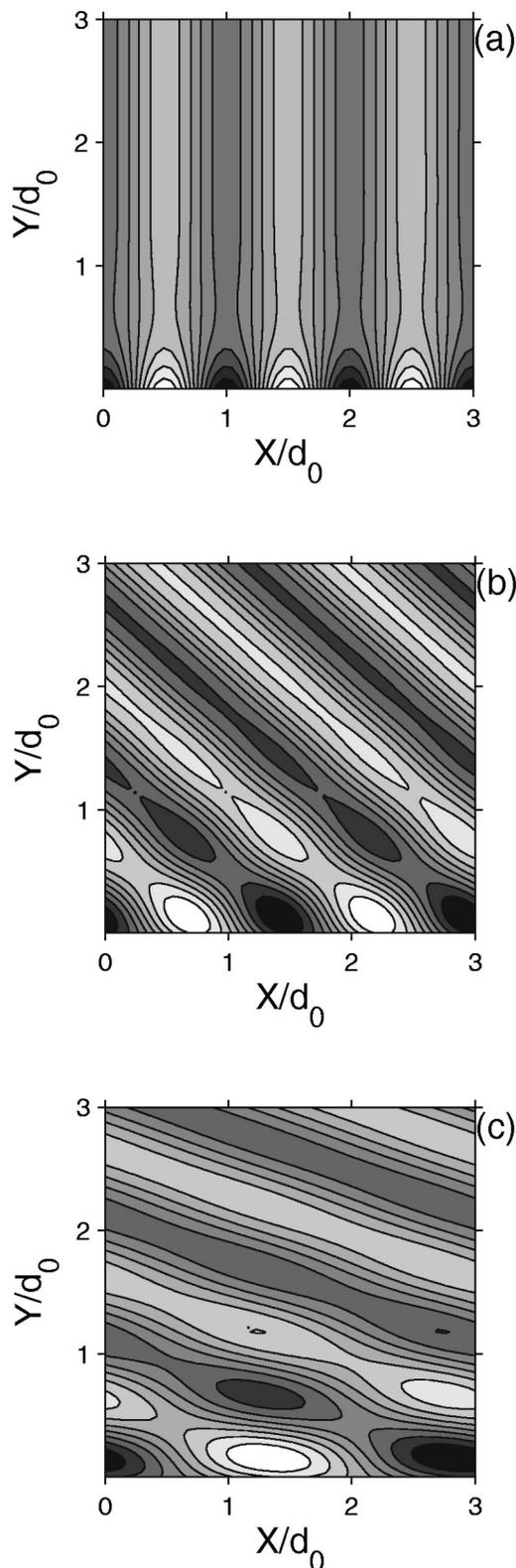


FIG. 2. Tilted lamellar phase between two parallel patterned surfaces. The surface patterning is modeled by the term $\sigma_q \cos(2\pi x/d_x)$. The lamellae tilt angle $\theta = \arccos(d_0/d_x)$ increase as the periodicity of the surface d_x increase: $\theta = 0$ for $d_x = d_0$ in (a), $\theta \approx 48.1^\circ$ for $d_x = \frac{3}{2}d_0$ in (b) and $\theta \approx 70.5^\circ$ for $d_x = 3d_0$ in (c). The correction field $\delta\phi$ is more important for large tilt angles, as it relieves the elastic stress near the surface. In the plots $\sigma_q/hq_0^3\phi_q = 1$ and the Flory parameter, $N\chi = 11.5$. In this and subsequent figures $\tau_s/hq_0^3 = 0.1$ and maximum (A-rich) and minimum (B-rich) values of ϕ correspond to white and black colors, respectively.

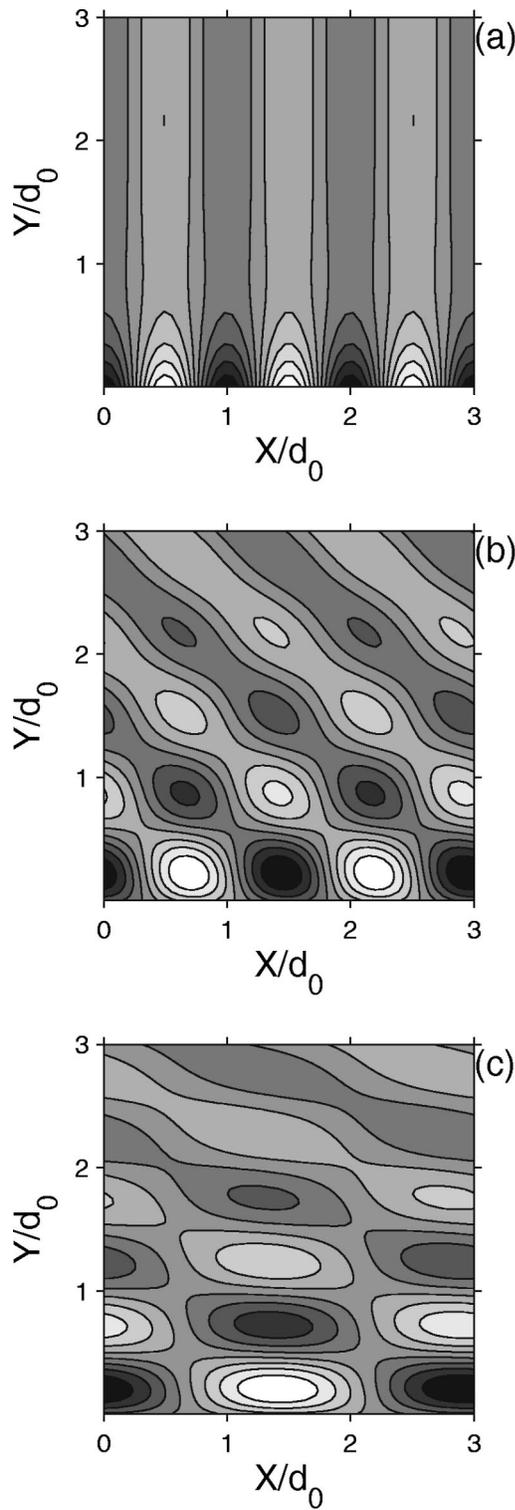


FIG. 3. The same sequence of tilt angles as in Fig. 2, but with the Flory parameter $N\chi=10.8$ much closer to its critical value $N\chi_c \approx 10.49$. The sinusoidally modulated surface field $\sigma(x)$ causes strong distortions of the tilted lamellar phase [parts (b) and (c)], even farther away from the surface.

surface fields give rise to strong chain stretching near the surface. Very large amplitude σ_q increases $\delta\phi$ on the expense of the bulk order parameter, ϕ_b , which remains constant. Note the similarity of these plots to the contour plots of Ref. 28.

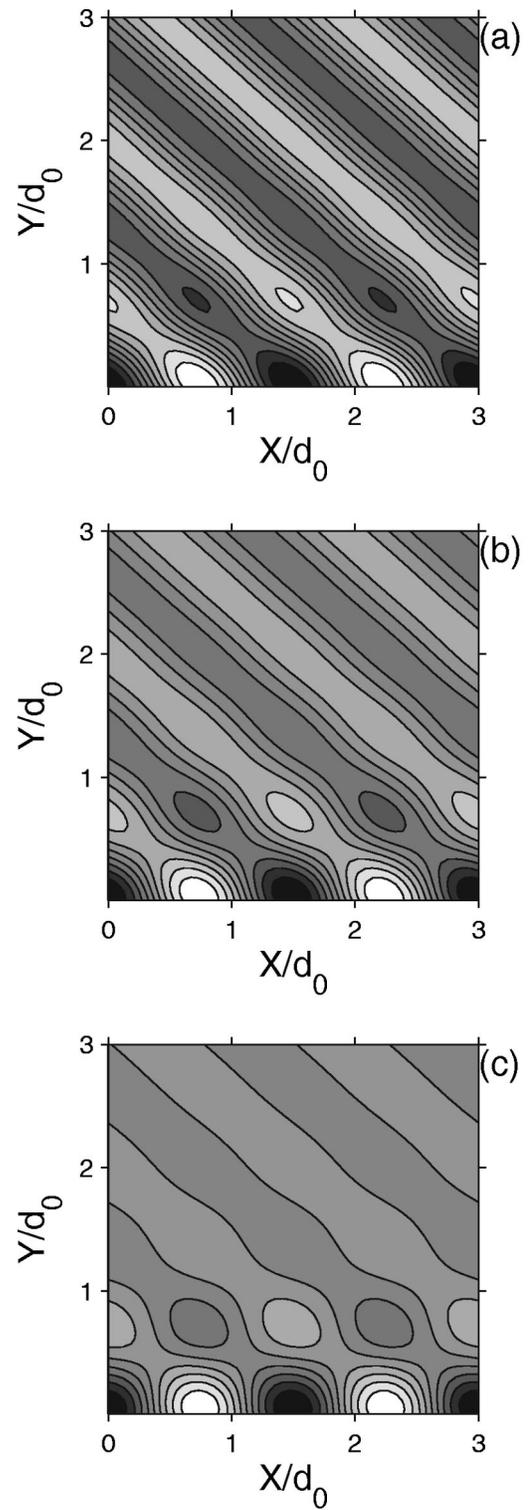


FIG. 4. Variation of the tilted lamellar morphology with σ_q , the amplitude of surface fields. The value of $\sigma_q/hq_0^3\phi_q$ is varied from 1 in (a), to 2 in (b), to 4 in (c), while the Flory parameter $N\chi=11 > N\chi_c$, and the repeat period $d_x = \frac{3}{2}d_0$ are held fixed.

IV. BCP THIN FILMS: ONE HOMOGENEOUS AND ONE PATTERNED SURFACE

Until now we have considered the semi-infinite problem of a BCP melt confined by one patterned surface. It is of

experimental and theoretical interest to study thin films of BCP when they are confined between a heterogeneous (patterned) surface and a second chemically homogeneous surface. This situation is encountered when a thin BCP is spread on a patterned surface. The second interface is the film/air interface (neglecting any height undulations), and is homogeneous. Usually the free surface has a lower surface tension with one of the two blocks. This bias can be modeled by adding a constant σ_0 term to the $\sigma(x)$ surface field. For simplicity, we assume that the $y = -L$ surface remains purely sinusoidal while the $y = L$ surface is attractive to one of the A/B blocks:

$$\begin{aligned} \sigma(x) &= \sigma_q \cos(q_x x), & \text{at } y = -L, \\ \sigma(x) &= \sigma_0, & \text{at } y = L. \end{aligned} \quad (22)$$

A neutral surface at $y = L$ is obtained as a special case with $\sigma_0 = 0$. The striped surface pattern is at $y = -L$ and the expression (14) for the bulk tilted phase is modified accordingly,

$$\phi_b = -\phi_q \cos[q_x x + q_y (y + L)]. \quad (23)$$

The surface free energy per unit length in the z -direction, Eq. (6), reads:

$$\begin{aligned} \mathcal{F}_s = \int dx \{ & \sigma_q \cos(q_x x) \phi(x, y = -L) + \tau_s \phi^2(x, y = -L) \\ & + \sigma_0 \phi(x, y = L) + \tau_s \phi^2(x, y = L) \}, \end{aligned} \quad (24)$$

where for simplicity the surface parameter τ_s is taken to be the same on the two boundaries $y = \pm L$.

For inter-surface separations $2L$ much larger than the bulk lamellar period, d_0 , the BCP morphology is similar to the one-surface case. Bringing the two surfaces closer together changes the melt morphology. In our formalism, $\phi_b(x, y)$, being the zero-order approximation, remains unchanged, while the correction $\delta\phi$ changes (recalling that the spatial variations of ϕ_b , Eq. (23), comes from the imposed tilt between the bulk lamellar phase and the surface direction). The homogeneous surface field at $y = L$ induces a lamellar layering parallel to the surface, since the two A/B blocks are covalently linked together. The simplest way to account for this layering effect is to extend Eq. (16) to include an x -independent term $w(y)$ in our ansatz for the order parameter:

$$\delta\phi(x, y) = g(y) \cos(q_x x) + w(y). \quad (25)$$

The free energy of the system is now written as a sum of two contributions:

$$\Delta\mathcal{F} = \int \{ \Delta F_g + \Delta F_w \} dy, \quad (26)$$

where ΔF_g is given by

$$\begin{aligned} \Delta F_g(y) = & -\frac{1}{2} \tau \cos^2(q_y y) g^2 + \frac{1}{4} h (q_y^2 g + g'')^2 \\ & + \frac{1}{2} [\sigma_q g + \tau_s (g^2 - 2\phi_q g)] \delta(y + L) \\ & + \frac{1}{2} \tau_s [g^2 - 2\phi_q \cos(2q_y L) g] \delta(y - L) \end{aligned} \quad (27)$$

and

$$\begin{aligned} \Delta F_w(y) = & -\frac{1}{2} \tau w^2 + \frac{1}{2} h (q_0^2 w + w'')^2 - \mu w \\ & + (\sigma_0 w + \tau_s w^2) \delta(y - L) + \tau_s w^2 \delta(y + L). \end{aligned} \quad (28)$$

We note here that in the expansion of the free energy to second order in $\delta\phi$ the mixed terms which couple w and g in $\Delta\mathcal{F}$ vanish. Again, the w -dependent terms in the surface free energy Eq. (24) are expressed via a Dirac delta function. The chemical potential μ couples only to $w(y)$ and not to $g(y)$, and fixes the total A/B ratio in the system as is imposed by the parameter f of the BCP chains (taken to be $f = \frac{1}{2}$ in this paper). The Euler–Lagrange equation corresponding to this free energy, Eq. (28), is a linear, ordinary fourth-order differential equation. Its solution can be written as a superposition of four exponential functions and a constant term:

$$w(y) = A_w e^{-k_w y} + B_w e^{k_w y} + A_w^* e^{-k_w^* y} + B_w^* e^{k_w^* y} + \text{const} \quad (29)$$

with

$$k_w^2 = -q_0^2 + \sqrt{\tau/h}. \quad (30)$$

The boundary conditions obeyed by $w(y)$ at $y = \pm L$ are

$$\begin{aligned} q_0^2 w(\pm L) + w''(\pm L) &= 0, \\ 2\tau_s w(-L) + h q_0^2 w'(-L) + h w'''(-L) &= 0, \\ \sigma_0 + 2\tau_s w(L) - h q_0^2 w'(L) - h w'''(L) &= 0, \end{aligned} \quad (31)$$

and those obeyed by $g(y)$ are similar to those in Eq. (20):

$$\begin{aligned} q_y^2 g(\pm L) + g''(\pm L) &= 0, \\ \sigma_q - 2\tau_s \phi_q + 2\tau_s g(-L) + h q_y^2 g'(-L) + h g'''(-L) &= 0, \\ -2\tau_s \phi_q \cos(2q_y L) + 2\tau_s g(L) - h q_y^2 g'(L) - h g'''(L) &= 0. \end{aligned} \quad (32)$$

In general the wavenumber k_w and the amplitudes A_w and B_w are complex. Expression (30) and (29) are identical to the zero q -mode response of a BCP in presence of a surface field for a system found above its ODT temperature in the disordered phase.^{8,16} Expression (29) has decaying modulations, as the wavevector k_w has both real and imaginary parts. The decay length $\xi = 1/\text{Re}(k_w)$ diverges as $(\chi - \chi_c)^{-1/2}$, while the modulation periodicity is slightly longer than that of the bulk lamellar phase (to order $\chi - \chi_c$). Lastly, the constant term in Eq. (29) [and the chemical potential μ in Eq. (28)] are determined by requiring that the total A/B ratio of monomers is conserved, $\int w(y) dy = 0$.

Figure 5 demonstrates two different thin-film morphologies, for a melt confined between two patterned surfaces, one at $y = -L = -2d_0$ and another which is homogeneously attractive to the B monomers at $y = L = 2d_0$. The BCP close to the lower and upper surfaces show different behavior, as the bottom surface is chemically patterned and the top is uniform. In Fig. 5(a) the top surface has a weak overall preference to the B monomers (in black), while in (b) this attraction is stronger, thus enhancing parallel lamellar ordering (layering).

This tilted lamellar phase confined by one homogeneous and one patterned surface is a generalization of the mixed

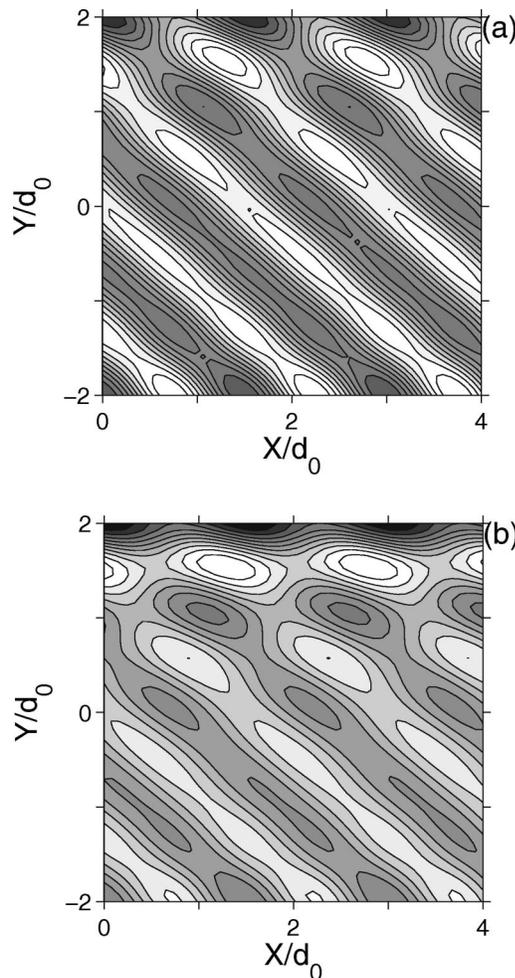


FIG. 5. A contour plot for a BCP melt between a top homogeneous surface at $y=L$, and a modulated bottom surface at $y=-L$. The inter-surface separation $2L$ is chosen to be $4d_0$ and the modulated surface amplitude is $\sigma_q/hq_0^3\phi_q=2$. The homogeneous top field is $\sigma_0/hq_0^3\phi_q=0.6$ in (a), and larger $\sigma_0/hq_0^3\phi_q=2$ in (b), preferring adsorption of the B monomers (black). The effect of this field is clearly seen close to the $y=L$ surface. In both plots the Flory parameter was chosen to be $N\chi=11$ and the repeat period of the bottom surface is $d=\frac{3}{2}d_0$.

(perpendicular and parallel) lamellar phase, usually referred to as L_M . The latter morphology occurs when the surface (imposed) periodicity d_x is equal to the bulk periodicity d_0 . This “T-junction” morphology, shown in Fig. 6, has perpendicular lamellae extending from the patterned surface. The homogeneous field at the opposite surface favors a parallel orientation of the lamellae. The crossover region between the two orientations is found in the middle of the film, and its morphology depends on the temperature, as can be seen by comparing (a) in which $N\chi=11$ with (b) where $N\chi=10.7$. In the latter case the effect of the homogeneous field is more evident, as parallel ordering extends from the top surface. For homogeneous surfaces and symmetric ($f=\frac{1}{2}$) BCP melts, these phases were considered unstable with respect to the L_{\parallel} and L_{\perp} phases,^{9,10} recalling that bulk T-junction defects are not usually found in experiments.²⁹ However, strong enough modulated surface fields stabilize the tilted lamellar phases, and in particular the L_M .

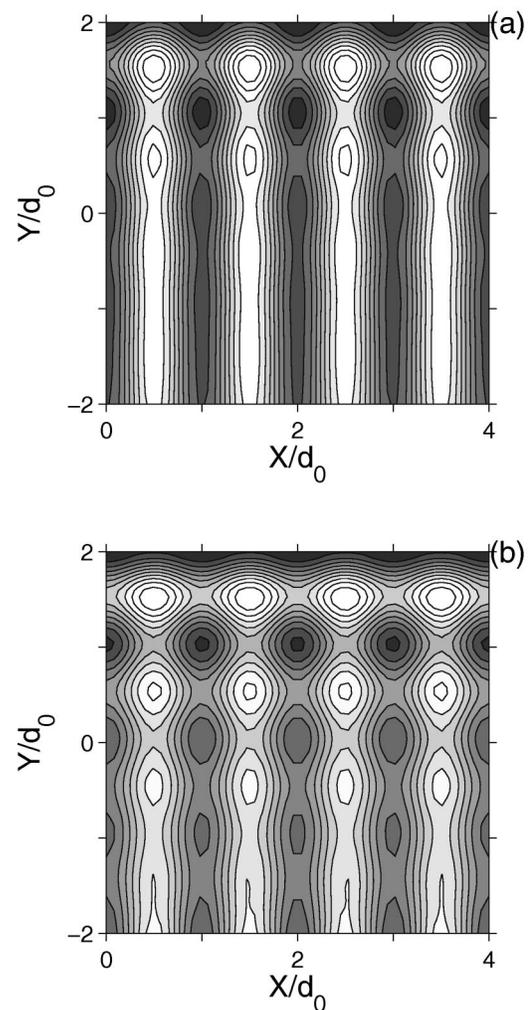


FIG. 6. A BCP confined film showing a crossover from perpendicular lamellae at the $y=-L=-2d_0$ surface to parallel lamellae at $y=L$. The pattern on the bottom surface, $\sigma(x)=\sigma_q\cos(q_0x)$, has the bulk periodicity d_0 , and amplitude $\sigma_q=2hq_0^3$, while the top surface ($y=L$) is homogeneously attractive to the B polymer (in black), $\sigma_0=4hq_0^3$. In (a) the Flory parameter is $N\chi=11$, while in (b) the temperature is closer to the ODT, $N\chi=10.7$.

It is important to check the self-consistency of our free energy variation by studying the difference between the film and bulk free energies. We show the free energy decrease as a function of surface separation $2L$ in Fig. 7, where $\Delta\mathcal{F}$ is taken from Eq. (26). The free energy has a characteristic oscillatory behavior as a function of surface separation $2L$. The period of these energy barriers is different from the bulk lamellar spacing d_0 , and depends on the tilt angle of the lamellae.

For separations larger than what is shown in Fig. 7 ($2L>8d_0$) the free energy difference tends to zero, since the correction field $\delta\phi$ has an important contribution only at a finite range away from the surface. As one approaches the ODT temperature the free energy difference $\Delta\mathcal{F}$ becomes larger compared to the bulk one because D , the width of surface induced ordering, increases and the bulk free energy decreases. Far from the ODT, i.e., in the strong segregation

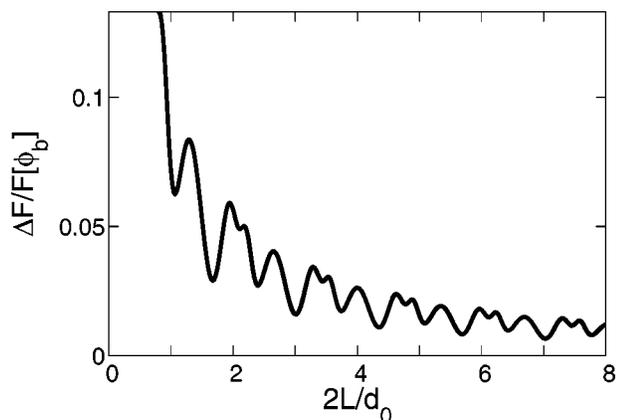


FIG. 7. The correction free energy $\Delta\mathcal{F}$ (divided by $\mathcal{F}[\phi_b]$, the bulk lamellar free energy) as a function of the film thickness $2L$. Lengths are scaled by the bulk lamellar period d_0 . The period of the oscillations characterizing the free energy $\Delta\mathcal{F}$ is different from d_0 , because the lamellae are tilted with respect to the surface. For all points in the plot, the modulated surface field at $y=-L$ has an amplitude $\sigma_q/hq_0^3\phi_q=0.5$ and a period $d_x=2\pi/q_x=\frac{3}{2}d_0$, while the surface field at $y=L$ is homogeneous with $\sigma_0=\sigma_q$. The Flory parameter is $N\chi=10.7$ and $\tau_s=0.7hq_0^3$.

limit, the bulk lamellar ordering is strong, and these surface corrections are important only for large surface fields σ .

V. CONCLUSION

We have employed a Ginzburg–Landau expansion of the free energy to study analytically the confinement effects of block copolymers between two surfaces as well as the interfacial behavior close to a single surface. For a BCP melt below its bulk ODT temperature, tilted lamellar phases are shown to exist between one patterned and one homogeneous surface if the chemical pattern is strong enough, and if no other defects exist inside the film.

Our approach consists of expressing the copolymer order parameter ϕ as a sum of two terms. The first term accounts for the bulk phase ϕ_b having the unperturbed periodicity d_0 , while the presumably small correction, $\delta\phi$, is entirely due to the surface and has the surface periodicity d_x .^{8,16} The extent of the commensurate region far from the surface is determined by the range of the amplitude function $g(y)$ introduced above, and it diverges at the ODT. This mean-field approach is valid close to the ODT, but not too close, where critical fluctuations are important.^{4,31} In addition, the linear response field $\delta\phi$ is assumed small, $\delta\phi\ll\phi_b$, and this can be justified if the surface field σ is not too large.

The deviation from the perfect diagonal lamellae ϕ_b relieves the BCP elastic energy near the surface, and induces an almost locally-parallel ordering. The analytic expressions presented here capture the effects Petera and Muthukumar investigated using the self-consistent field theory.²⁸ Moreover, in the weak segregation limit studied here, $\chi\approx\chi_c$, the energetic difference between the lamellar and the disordered phases is small, leading to lamellae which are more amenable to deformations. In this weak segregation regime the correction to the order parameter, $\delta\phi$, gives an important contribution to the free energy (as can be seen quantitatively in Fig. 7), and to the resulting morphology. This description,

however, is accurate only when the surface interactions at $y=-L$ are large, and the overall state is that of the tilted lamellae morphology.

We find a similarity between thin BCP films and that of the symmetric tilt grain boundaries. In the latter system, the tilt angle is determined by the externally imposed relative orientation of the two grains. In both systems, packing frustration of the polymer chains occur at the interface. However, the BCP film we consider here has a richer behavior because the model contains a real surface interacting chemically with the chains. The analogy shows that the width D of surface deformation scales as $D\sim(1-d_0/d_x)^{-1/2}$, for $1-d_0/d_x\ll 1$.

We consider in particular the case where one of the surfaces uniformly prefers one of the blocks. This can be, for example, the free surface of the film (polymer/air interface) and is accommodated in our model by considering an additional response field, $w(y)$. Tilted lamellae appear at the patterned surface while parallel lamellae are created at the opposite surface, generalizing the mixed lamellar phases L_M found for homogeneous surfaces.^{11,13} Morphologies similar to T-junction defects are then obtained when the pattern period is the natural period. Although the energetic penalty for a T-junction in the bulk is high, chemically interacting surfaces can stabilize these structures.

The field $w(y)$ is also used to describe the perpendicular L_\perp and parallel oriented L_\parallel lamellar phases found in the presence of uniform surfaces. The free energies of these phases change considerably under the influence of the surface fields, and hence the features of the phase diagram may be different from that of the strong segregation regime.¹⁴

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