Diblock copolymer ordering induced by patterned surfaces

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Abstract. – We use a Ginzburg-Landau free-energy functional to investigate diblock copolymer morphologies when the copolymer melt interacts with one surface or is confined between two chemically patterned surfaces. For temperatures above the order-disorder transition a complete linear response description of the copolymer melt is given, in terms of an arbitrary two-dimensional surface pattern. The appearance of order in the direction parallel to the surface is found as a result of the order in the perpendicular direction. Below the order-disorder transition and in a thin-film geometry, our procedure enables an analytic calculation of distorted perpendicular and tilted lamellar phases in the presence of uniform or striped surface fields.

Block copolymers (BCP) are macromolecules made up of two or more chemically distinct subunits, or blocks, covalently bonded together. The usual (macro-) phase separation occurring for two immiscible species is not possible for BCP because of the covalent bond between the blocks. The most studied BCP are the diblocks, for which the phase diagram is quite well understood [1–6], and was found to consist of disordered, lamellar, hexagonal and cubic micro-phases with characteristic length scale usually in the range of dozens of nanometers. The prevailing morphologies depend on three parameters: the Flory parameter χ, characterizing the incompatibility between the two blocks, the polymerization degree of the chain N, and the fraction $f = N_A/N$ of the A block in a chain of $N = N_A + N_B$ monomers. For high enough temperatures the system is found in its disordered state. For symmetric melts ($f = 1/2$) lowering the temperature (or, equivalently, raising χ) results in a phase transition to the lamellar phase through the order-disorder transition (ODT) point. For asymmetric melts ($f \neq 1/2$) the ordered phases can have, in addition, hexagonal (cylindrical) or cubic symmetries [1–6].

The technological importance of copolymer thin films is prominent in diverse fields, such as in fabrication of nanolithographic templates [7], waveguides, anti-reflection coating for optical surfaces [8] and dielectric mirrors [9]. Therefore, it is highly desired to acquire a better understanding of the copolymer behavior in the presence of chemically patterned surfaces. Theoretical [10–20] and experimental [21–25] studies have been carried out in order to explore

how the BCP film thickness, the range and strength of the uniform surface interactions, as well as the bulk parameters χ, N and f, compete to produce a rich interfacial behavior. Below the ODT, these studies [15, 17, 19] revealed parallel, perpendicular and mixed lamellar phases, the apparent morphology being the one that optimizes interaction with the surface and periodicity frustration. Alignment of the lamellae can also be achieved through the coupling of electric fields to local dielectric constant variations [26], or by shear [27].

Let us consider first a BCP melt in its disordered phase (above the bulk ODT temperature) and confined by one or two flat, chemically patterned surfaces. Although the bulk BCP is disordered above the ODT, there is an oscillatory decay of the A-B correlations and surface-induced ordering is quite complex. In the vicinity of the ODT this ordering can become long range leading to a strong effect. Defining the order parameter $\phi(\boldsymbol{r}) \equiv \phi_{\rm A}(\boldsymbol{r}) - f$ as the deviation of the A monomer local concentration from its average, the free energy (in units of the thermal energy $k_{\rm B}T$) can be written as

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

$d_0 = 2\pi/q_0$ is the fundamental periodicity in the system, and is expressed by the polymer radius of gyration $R_{\rm g}$, through $q_0 \simeq 1.95/R_{\rm g}$. In addition, $\tau = 2\rho N\left(\chi_{\rm c} - \chi\right)$, $h = 1.5\rho c^2 R_{\rm g}^2/q_0^2$ and μ is the chemical potential. The second length scale in the system is determined by the ratio of two parameters, $(\tau/h)^{-1/4} \sim (N\chi_{\rm c} - N\chi)^{-1/4}$, and it characterizes the decay of surface-induced modulations. The Flory parameter χ measures the distance from the ODT point, having the value $\chi_{\rm c} \simeq 10.49/N$. Finally, $\rho = 1/Na^3$ is the chain density per unit volume, and c and u/ρ are dimensionless constants of order unity [4].

This and similar types of free energy have been used successfully to describe spatially modulated phases [28–30], with applications to amphiphilic systems [31, 32], diblock copolymers [3–5, 33, 34], Langmuir films [35] and magnetic (garnet) films [36]. The free energy, eq. (1), describes a system in the disordered phase having a uniform $\phi = 0$ for $\chi < \chi_{\rm c}$, while for $\chi > \chi_{\rm c}$ (but in the vicinity of $\chi_{\rm c}$), the system is in the lamellar phase and is described approximately by a single q-mode $\phi = \phi_q \exp[i\boldsymbol{q}_0 \cdot \boldsymbol{r}]$. The use of eq. (1) limits us to a region of the phase diagram close enough to the critical point where the expansion in powers of ϕ and its derivatives is valid, but not too close to it, because then critical fluctuations are important [1].

The presence of chemically heterogeneous surfaces is modeled by adding a short-range surface interaction to the free energy,

$$F_{\rm s} = \int \mathrm{d}^2\boldsymbol{r}_{\rm s} \left(\sigma(\boldsymbol{r}_{\rm s})\phi(\boldsymbol{r}_{\rm s}) + \tau_{\rm s}\phi^2(\boldsymbol{r}_{\rm s}) \right) \,, \tag{2}$$

where the vector $\boldsymbol{r} = \boldsymbol{r}_{\rm s}$ defines the position of the confining surfaces. The surface field $\sigma(\boldsymbol{r}_{\rm s})$ has an arbitrary but fixed spatial variation and is coupled linearly to the BCP surface concentration $\phi(\boldsymbol{r}_{\rm s})$. Preferential adsorption of the A block is modeled by a constant $\sigma < 0$ surface field, resulting in parallel-oriented layers (a perpendicular orientation of the chains). Control over the magnitude of this surface field can be achieved by coating the substrate with carefully prepared random copolymers [24, 25]. If the pattern is spatially modulated, $\sigma(\boldsymbol{r}_{\rm s}) \neq 0$, then the A and B blocks are attracted to different regions of the surface. The coefficient of the ϕ^2 term in eq. (2) is taken to be a constant surface correction to the Flory parameter χ [10, 11]. A positive $\tau_{\rm s}$ coefficient corresponds to a suppression of surface segregation of the A and B monomers.

We consider first the semi-infinite system of polymer melt in contact with a single flat surface given by $\boldsymbol{r}_{\rm s} = (x, y = 0, z)$. The ordering effect is expressed in terms of the correction

to the order parameter $\delta\phi(\boldsymbol{r}) = \phi - \phi_\mathrm{b}$ about its bulk value ϕ_b. This correction vanishes in the bulk, $\lim_{y\to\infty}\delta\phi = 0$, because of the finite range of surface interactions. Moreover, the correction should preserve the condition of fixed A/B ratio, namely $\int \delta\phi(\mathbf{r})\mathrm{d}^3r = 0$. The free energy can be expanded about the bulk value $F[\phi_\mathrm{b}]$ to second order in $\delta\phi$: $F = F[\phi_\mathrm{b}] + \Delta F$, with

$$
\begin{aligned}
\Delta F = {} & \int \left\{ \left[(\tau + hq_0^4)\phi_\mathrm{b} + hq_0^2\nabla^2\phi_\mathrm{b} + \frac{1}{6}u\phi_\mathrm{b}^3 - \mu \right] \delta\phi + \right. \\
& \left. + \frac{1}{2}(\tau + \frac{1}{2}u\phi_\mathrm{b}^2)\delta\phi^2 + \frac{1}{2}h\left[\left(q_0^2 + \nabla^2 \right)\delta\phi \right]^2 \right\} \mathrm{d}^3\boldsymbol{r} + \\
& + \int \{ \sigma(x,z)\delta\phi_\mathrm{s} + \tau_\mathrm{s} \left(2\phi_\mathrm{b}\delta\phi_\mathrm{s} + \delta\phi_\mathrm{s}^2 \right) \}\mathrm{d}x\mathrm{d}z \,.
\end{aligned}
\tag{3}
$$

$\delta\phi_\mathrm{s} = \delta\phi(x,0,z)$ is the surface value of $\delta\phi$. The surface chemical pattern $\sigma(\boldsymbol{r}_\mathrm{s}) = \sigma(x,z)$ can be decomposed in terms of its q-modes $\sigma(x,z) = \sum_{\boldsymbol{q}} \sigma_{\boldsymbol{q}} \exp[i\,(q_x x + q_z z)]$, where $\boldsymbol{q} \equiv (q_x, q_z)$, and $\sigma_{\boldsymbol{q}}$ is the mode amplitude. Similarly, the correction field is $\delta\phi(x,y,z) = \sum_{\boldsymbol{q}} \delta\phi_{\boldsymbol{q}}(y) \exp[i(q_x x + q_z z)]$, and is substituted in eq. (3). We will first consider a system found above the ODT temperature, in the disordered phase. In this case $\phi_\mathrm{b} = 0$, and the x and z integration of the free energy, eq. (3), is carried out explicitly. Then, applying a variational principle with respect to $\delta\phi_{\boldsymbol{q}}$ results in the following differential equation:

$$
\left(\tau/h + \left(q^2 - q_0^2 \right)^2 \right) \delta\phi_{\boldsymbol{q}} + 2(q_0^2 - q^2)\delta\phi_{\boldsymbol{q}}'' + \delta\phi_{\boldsymbol{q}}'''' = 0 \,.
\tag{4}
$$

This ordinary differential equation is linear and of fourth order. In the semi-infinite geometry, $y > 0$, the solution to eq. (4) has an exponential form $\delta\phi_{\boldsymbol{q}}(y) = A_{\boldsymbol{q}}\exp[-k_{\boldsymbol{q}}y] + B_{\boldsymbol{q}}\exp[-k_{\boldsymbol{q}}^*y]$, where $k_{\boldsymbol{q}}$ is given by

$$
\begin{aligned}
k_{\boldsymbol{q}}^2 &= q^2 - q_0^2 + i\sqrt{\tau/h} \\
&= q^2 - q_0^2 + i\alpha \left(N\chi_\mathrm{c} - N\chi \right)^{1/2} \,.
\end{aligned}
\tag{5}
$$

Out of the four complex roots for $k_{\boldsymbol{q}}$, the two with $\mathrm{Re}(k_q) < 0$ diverge at $y \to \infty$ and are discarded. From the requirement of fixed A/B ratio it follows that the chemical potential is $\mu = 0$. For numerical purposes and in all plots we set the fundamental monomer length as $a = 1$, and choose in eq. (1) $c = u/\rho = 1$ to give $\alpha \simeq 0.59q_0^2$. The values of $\xi_q = 1/\mathrm{Re}(k_{\boldsymbol{q}})$ and $\lambda_q = 1/\mathrm{Im}(k_{\boldsymbol{q}})$ correspond to the exponential decay and oscillation lengths of the q-modes, respectively. For fixed χ, ξ_q decreases and λ_q increases with increasing q. Similar behavior was found by Petera and Muthukumar [18], using a different free-energy functional [2]. Close to the ODT (but within the range of validity of the model), and for q-modes such that $q > q_0$ we find finite ξ_q and $\lambda_q \sim (\chi_\mathrm{c} - \chi)^{-1/2}$. However, all q-modes in the band $0 < q < q_0$ are equally "active", i.e., these modes decay to zero very slowly in the vicinity of the ODT as $y \to \infty$: $\xi_q \sim (\chi_\mathrm{c} - \chi)^{-1/2}$ and λ_q is finite. Therefore, the propagation of the surface imprint (pattern) of q-modes with $q < q_0$ into the bulk can persist to long distances, in contrast to surface patterns with $q > q_0$ which persist only close to the surface. The $q = q_0$ mode has both lengths ξ_q, λ_q diverging as $(\chi_\mathrm{c} - \chi)^{-1/4}$ for $\chi \to \chi_\mathrm{c}$.

The boundary conditions at $y = 0$ for $\delta\phi_{\boldsymbol{q}}$ are

$$
\delta\phi_{\boldsymbol{q}}''(0) + \left(q_0^2 - q^2 \right) \delta\phi_{\boldsymbol{q}}(0) = 0 \,,
\tag{6}
$$

$$
\sigma_{\boldsymbol{q}}/h + 2\tau_\mathrm{s}\delta\phi_{\boldsymbol{q}}(0)/h + \left(q_0^2 - q^2 \right) \delta\phi_{\boldsymbol{q}}'(0) + \delta\phi_{\boldsymbol{q}}'''(0) = 0 \,.
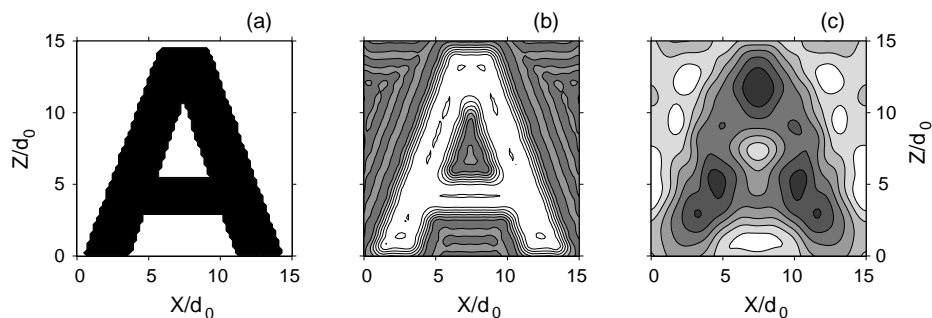\tag{7}
$$

Fig. 1 – Contour plots of the diblock copolymer order parameter depicting slices parallel to the $y = 0$ surface. (a) The surface pattern at $y = 0$, chosen in the shape of the "A" letter of size $15d_0 \times 15d_0$. Inside the letter "A" $\sigma = 1$, while outside $\sigma = 0$. In (b) the BCP morphology is shown for $y = 0.5d_0$, and in (c) for $y = 12d_0$. For planes separated by a half integer number of d_0, an A↔B interchange of monomers occurs (compare (b) to (a) and (c)). The order propagating in the perpendicular direction induces order in a direction parallel to the surface. This is clearly seen in (b) where lamellae form parallel to the edges of the "A" letter. The Flory parameter is $\chi N = 10.3$ and seven gray scales are used to maximize the image contrast. All lengths are scaled by the lamellar period d_0, and the parameters chosen in eq. (1) are: $N = 1000$, $R_g^2 = \frac{1}{6} N a^2$, $a = c = u/\rho = 1$ and $\tau_s = 0.03$. These values are used in figs. 2, 3 as well.

The amplitude A_q is found to be $A_q = -\sigma_q \left(4\tau_s + 2\,\mathrm{Im}(k_q)\sqrt{\tau h} \right)^{-1}$. Thus, in cases where the surface orders at the same temperature as the bulk, $\tau_s = 0$, the copolymer response diverges upon approaching the critical point as $(N\chi_c - N\chi)^{-1/2}$.

With our method, any two-dimensional chemical pattern $\sigma(x, z)$ can be modeled. For surface feature size larger than d_0, the characteristic copolymer length, the melt can propagate the chemical surface pattern into the bulk. This is clearly seen in fig. 1, where the surface
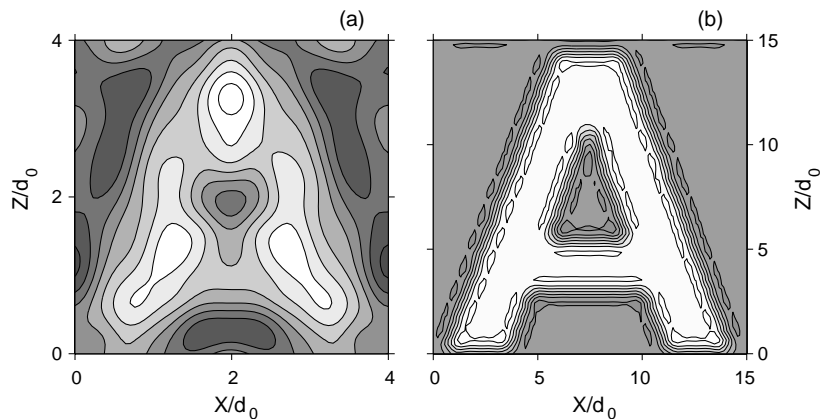

Fig. 2 – Contour plots as in fig. 1(b) ($y = 0.5d_0$), but in (a) the surface pattern is reduced to a size of $4d_0 \times 4d_0$. Note that the surface cannot induce a bulk ordering when its pattern size is close to d_0 or smaller. In (b) the temperature is higher, $\chi N = 9.5$, and the lamellar features along the letter are less prominent than in fig. 1(b).
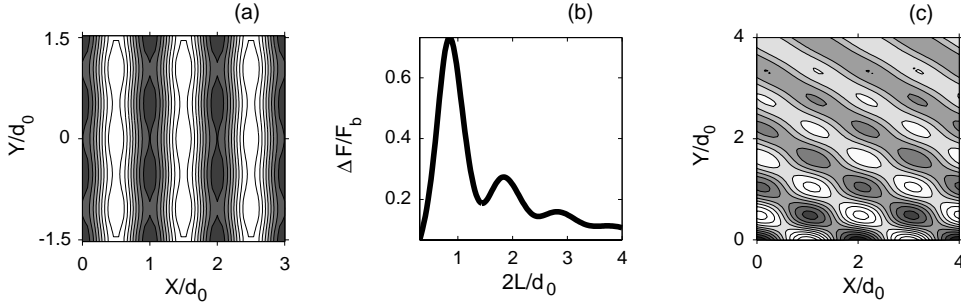
Fig. 3 – (a) Perpendicular lamellar phase between two (top and bottom) surfaces below the ODT ($\chi N = 10.7$). The two surfaces at $y = \pm L$ have equal surface fields, $\sigma^+ = \sigma^- = 0.07$, preferring the B block (in black). (b) The oscillatory character of the correction free energy $\Delta F < 0$ (eq. (3)) of the symmetric system in (a), as a function of surface separation $2L$. ΔF is divided by the bulk lamellar free energy $F_{\rm b} < 0$, and it decays to zero for $L \to \infty$. (c) Tilted lamellar phase occurring for a single sinusoidally patterned surface of period $d > d_0$ at $y = 0$. The lamellae gain interfacial energy by overlapping with the surface pattern. The Flory parameter is $\chi N = 11$ and the surface periodicity is chosen as $d/d_0 = 2$ giving a tilt angle of $\theta = 30°$.

pattern separating A regions and B regions is chosen arbitrarily to have the shape of the letter "A" of size $15d_0 \times 15d_0$. The order propagating perpendicular to the surface, fig. 1, also induces order in a parallel direction, where lamellae appear oriented along the long edges of the letter. This ordering decays exponentially in the lateral direction, with decay length determined by the surface q-modes. The shading of the contours in (b) is approximately opposite to that of (a) and (c) indicating a reversal of the pattern; this is expected for two planes separated by a half-integer number of d_0, a distance for which an A$\leftrightarrow$B interchange of monomers occurs. The distance from the surface at which the pattern completely fades out depends on the surface Fourier components: each q-mode decays as dictated by eq. (5), and the distant image is a superposition of all modes. In (c) the pattern is almost washed out at a distance $12d_0$ from the surface. Figure 2(a) is similar to fig. 1(b) (with $y = 0.5d_0$), but we scaled down the "A" pattern so that its size is $4d_0 \times 4d_0$. For surface feature size smaller than d_0, the melt cannot follow the surface pattern, and the morphology is blurred even very close to the surface. As one goes deeper into the disordered phase (lowering χ), the lamellar features are less apparent, as is seen in fig. 2(b) for which $\chi N = 9.5$ and all other parameters are taken as in fig. 1(b).

Our treatment can be generalized to handle a thin BCP film of thickness $2L$ confined between two chemically patterned surfaces. The two corresponding surface patterns (located at $y = \pm L$) are defined by two surface fields $\sigma^\pm(x, z) = \sum_{\boldsymbol{q}} \sigma_{\boldsymbol{q}}^\pm \exp\left[i\left(q_x x + q_z z\right)\right]$. The form of the response function $\delta\phi$ is required now to satisfy four boundary conditions (similar to eqs. (6) and (7)), two on each surface. For very large separation $2L$, the melt orders close to the $y = \pm L$ surfaces, while the middle of the film, $y \approx 0$, is in its disordered state. As the inter-surface separation decreases, the ordered layers close to the two surfaces start to overlap.

We briefly mention results for a thin-film BCP below its bulk ODT temperature [37], where the two surface fields $\sigma^\pm$ at $y = \pm L$ are taken to be uniform. Their values can be positive or negative depending on their preference to the A and B blocks. The free energy, eq. (3), expresses a correction to a lamellar phase perpendicular to the surface. The correction field $\delta\phi(y)$ has the form $\mathrm{Re}[A_0 \exp[-k_0 y] + B_0 \exp[-k_0^* y] + \mathrm{const}]$. A similar perturbed lamellar phase was found in the strong or intermediate segregation regimes [15,19]. However, close to

the ODT the lamellar deformation near the surface changes the free energy considerably. This is seen in fig. 3(a) for the symmetric case, $\sigma^+ = \sigma^-$. The B monomers (in black) are attracted to both surfaces. The oscillatory excess free energy $\Delta F < 0$ is shown in (b) as a function of the separation $2L$ between the surfaces, indicating that the deformation $\delta\phi$ indeed lowers the total free energy. In (c) a semi-infinite system is shown, with one sinusoidally patterned surface of period d at $y = 0$. The lamellae appear tilted with an angle $\theta = \arcsin(d_0/d)$ with respect to the surface, in agreement with ref. [18]. Close to the surface the deformation may be very large.

In summary, we show a simple method to find the surface effects in confined diblock copolymers. The free energy is expanded to second order around a bulk (ordered or disordered) phase. Above the ODT we obtain a master equation for the response of copolymer melt to an arbitrary two-dimensional surface pattern. These two-dimensional patterns have not been considered previously [18] and show a rich behavior as the BCP order parameter replicates (to some extent) the surface pattern. In order to transfer a pattern from the surface to the bulk, or from one surface to another via a BCP film, it is important to control the thermodynamic conditions, and in particular, how close we are to the ODT. Two opposite trends should be taken into account. On the one hand, far from the ODT, the required surface fields may be large. On the other hand, close to the ODT, high q-modes decay much faster than low q-modes, resulting in a distorted pattern. Below the ODT we find the profile and energy of the distorted perpendicular lamellar phase as a function of the surface fields and film thickness. When the surfaces are chemically modulated tilted lamellar phases are stabilized [37].

Surface behavior of BCP or thin films of BCP confined between two surfaces may be used in many applications. For example, surface patterns can be used to generate a desired morphology inside a BCP film. Then, one of the two components is removed leaving behind a pre-designed porous material with controlled morphology.

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