

Surface-Induced Lamellar Ordering in a Hexagonal Phase of Diblock Copolymers

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ABSTRACT: We study theoretically the hexagonal phase of diblock copolymer melts and determine the conditions under which a region of lamellar ordering is induced near a flat surface. In the weak segregation limit we employ a Landau-Ginzburg mean-field theory to describe the interfacial structure of the ordered hexagonal phase. The surface field, proportional to the differential affinity of blocks A and B to the surface, couples to the wave component perpendicular to the interface and increases the lamellar character of the ordered structure close to the surface. The extent of the region where this lamellar character predominates diverges logarithmically when the bulk hexagonal-lamellar transition is approached. In the strong segregation limit we find that the lamellar region exists provided that the surface field is larger than some critical value, readily obtainable in experiments. We find that the extent of the region of lamellar ordering also increases logarithmically with decreasing free energy difference between the hexagonal and lamellar phases.

I. Introduction

It is now well established that, for temperatures below the order-disorder temperature T_{ODT} , diblock copolymers self-assemble spontaneously in the melt to form ordered phases consisting of sheets (the lamellar phase), rods (the hexagonal phase), spheres (the cubic phase), or multi-connected, bicontinuous arrangements of copolymers with cubic or more exotic symmetries.^{1,2} This self-assembly is driven by the immiscibility of the two different chemical components of the polymer, denoted by A and B. By forming a segregated phase, the system minimizes the number of A-B contacts, thereby saving energy which offsets the corresponding loss of polymer entropy. In a system containing lamellar layers, for example, each lamella can be viewed as a layer, with normal in the z -direction (say), where the concentration of one of the copolymer blocks is predominant. The layer itself is liquid and retains translational symmetry in the x - y plane. In the so-called weak segregation limit the excess of one of the species varies smoothly over the layer depth; see Figure 1a. On the contrary, in the strong segregation limit, well below the transition temperature, there is a sharp interface between alternate regions of almost pure A or B blocks; see Figure 1b. In the hexagonal region of the phase diagram the diblock copolymers are disposed into cylindrical infinite aggregates which pack hexagonally in the plane perpendicular to the axis of the cylinders. In the other phases the polymers pack in a similar manner, according to the phase symmetry.

We consider here a monodisperse melt of linear diblock copolymers with total degree of polymerization N , made up of one A-block of N_A monomers joined to one B-block of $N - N_A$ monomers. The bulk phase behavior of these copolymers has been shown to be sensitive to two parameters:^{3,4} (i) χN , where χ is the Flory incompatibility parameter between A and B polymers, in $k_B T$ units, and (ii) the molecular asymmetry parameter $f \equiv N_A/N$. For symmetric ($f = 1/2$) diblock copolymers, for instance, the mean-field theory³ predicts the formation of a lamellar phase at temperatures where $\chi N = (\chi N)_s \approx 10.49$ (better

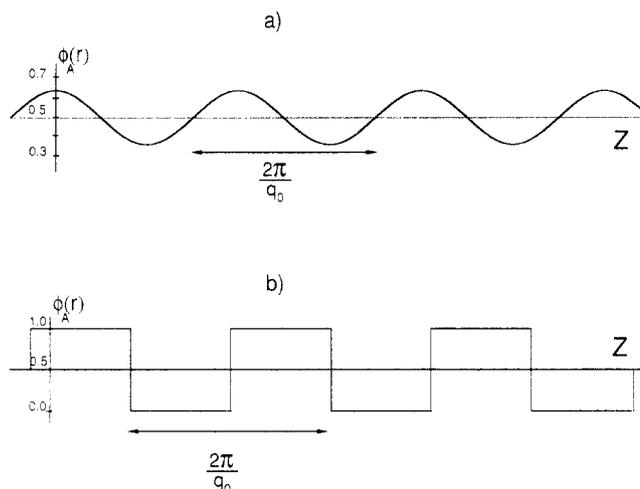


Figure 1. Representation of the density profile of the A monomers for a lamellar stack of symmetric A-B diblock copolymers. (a) Weak segregation limit. The maximum double amplitude is in general far from unity. The base line corresponds to the sample average content of A monomers. (b) Strong segregation limit. The bottom line is zero, the B monomers being completely excluded from the A-rich region.

estimates can be obtained by properly taking into account the role of fluctuations⁵). For asymmetric copolymers ($f \neq 1/2$) cubic and hexagonal structures are predicted to form at lower temperatures, *i.e.*, at higher values of χN . Well below the transition temperature, in the so-called strong segregation limit, the transition from one to the other phase is mainly driven by f , the asymmetry parameter. The theory of Semenov⁴ predicts that the hexagonal phase is found for $0.12 < f < 0.28$ (where we choose $f \leq 0.5$ without loss of generality), whereas the lamellar and cubic phases are found for $f > 0.28$ and $f < 0.12$, respectively. In the present work we study the extent of surface-induced lamellar ordering in copolymer melts where the stable phase in the bulk is hexagonal. The presence of a flat surface with a differential affinity for blocks A and B has already been shown to induce a region of lamellar ordering in copolymer systems above the ordering temperature.⁶⁻¹⁰ In the next section we investigate how this affinity changes also the interfacial structure of a weakly ordered hexagonal phase. The limit

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of strong segregation is studied in section III. Section IV is devoted to discussion of the results.

II. Weak Segregation

In this section we study the interfacial structure of a hexagonal phase of A-B diblock copolymers close to the ordering transition. In this limit the system can be described by a Landau-Ginzburg expansion of the free energy as a function of the local average excess concentration of (say) monomer A, $\psi(\mathbf{r}) = \phi_A(\mathbf{r}) - \langle \phi_A \rangle$

$$F[\psi_q]N = \frac{1}{2!} \int_q S(q)^{-1} \psi_q \psi_{-q} - \frac{\mu}{3!} \int_q \int_{q'} \psi_q \psi_{q'} \psi_{-q-q'} + \frac{\lambda}{4!} \int_q \int_{q'} \int_{q''} \psi_q \psi_{q'} \psi_{q''} \psi_{-q-q'-q''} \quad (1)$$

where $S(q = |\mathbf{q}|)$ is the Fourier transform of the two-point correlation function in the disordered homogeneous phase, and ψ_q is the q -Fourier component of the order parameter ψ . The factor of N on the left-hand side of eq 1 ensures that all the coefficients are of order unity (we will absorb the factor N in the definition of all the free energies written below). The third- and fourth-order coefficients μ and λ are simple q -independent (but f -dependent) approximations for the vertex functions of the thermodynamic potential. For symmetric systems where $f = 1$ the third-order coefficient μ vanishes. The (arbitrary) choice of the sign of the third-order term fixes conveniently the phase of the hexagonal structure at the surface. Close to the order-disorder transition the susceptibility $S(q)$ is strongly peaked around some vector q_0 and can be approximated by

$$S^{-1}(q) = \tau + c(q^2 - q_0^2)^2 \quad (2)$$

with an effective temperature τ which depends on the A-B interaction parameter χ , $\tau = 2(\chi N)_s - 2(\chi N)$. When the effective temperature τ vanishes (one has for instance, for symmetric ($f = 1/2$) diblocks, $\chi N = (\chi N)_s = 10.49$), the susceptibility $S(q)$ diverges for values of the wavevector on the reciprocal space shell $|\mathbf{q}| = q_0$. The typical wavelength associated with the vector q_0 is of order of $R = (Na^2/6)^{1/2}$, the radius of gyration of the polymer chain, a being the size of one monomer. The constant c is related to the curvature of the scattering function at its maximum. A good approximation^{5,11,12} for these quantities is provided by the relations $q_0^2 R^2 = [3/f(1-f)]^{1/2}$ and $cq_0^2 = R^2/(2f(1-f))$. The other two parameters entering in the free energy are also functions of the asymmetry f . In particular μ vanishes for symmetric diblock copolymers where $f = 1/2$. Values for these parameters can be found in refs 3 and 5. The Landau-Ginzburg functional in eq 1 predicts the formation of three ordered phases for diblock copolymers: body-centered cubic, hexagonal, and lamellar (smectic). We will investigate below the temperature region where the stable phase is hexagonal, with special attention to the neighborhood of the hexagonal to lamellar transition temperature.

The bulk hexagonal phase can be described by a first-harmonic expansion of the order parameter:

$$\psi(z,y) = 2a_1 \cos\{q_0 z\} + 2a_2 \cos\left\{q_0 \frac{3^{1/2}y - z}{2}\right\} + 2a_3 \cos\left\{-q_0 \frac{3^{1/2}y + z}{2}\right\} \quad (3)$$

which leads to the free-energy density

$$F = \tau(a_1^2 + a_2^2 + a_3^2) - 2\mu a_1 a_2 a_3 + \frac{\lambda}{4}(a_1^4 + a_2^4 + a_3^4 + 4a_1^2 a_2^2 + 4a_2^2 a_3^2 + 4a_1^2 a_3^2) \quad (4)$$

In the bulk one has $a_1 = a_2 = a_3 = a_h$ corresponding to the free-energy density

$$F_h = 3\tau a_h^2 - 2\mu a_h^3 + \frac{15}{4}\lambda a_h^4 \quad (5)$$

The density of a lamellar phase can also be obtained from eq 3 by setting $a_1 = a_l$ and $a_2 = a_3 = 0$. The associated free-energy density reads

$$F_l = \tau a_l^2 + \frac{1}{4}\lambda a_l^4 \quad (6)$$

It is convenient to reduce the free-energy expressions and amplitudes in the following manner:

$$F_h = \frac{\mu^4}{\lambda^3} \left[-3\alpha Y^2 - 2Y^3 + \frac{15}{4}Y^4 \right] \quad (7)$$

$$F_l = \frac{\mu^4}{\lambda^3} \left[-\alpha X^2 + \frac{1}{4}X^4 \right] \quad (8)$$

where the amplitudes and temperature have been normalized by $\tau = -\alpha\mu^2/\lambda$, and $a_h = Y\mu/\lambda$, and $a_l = X\mu/\lambda$. The bulk equilibrium values of the amplitudes are given by

$$X = (2\alpha)^{1/2} \\ Y = \frac{1 + (1 + 10\alpha)^{1/2}}{5} \quad (9)$$

The low-temperature phase is the lamellar phase; the transition temperature from hexagonal to lamellar is located at $\alpha = (7 + 3\sqrt{6})/5 \simeq 2.87$. Note that the hexagonal phase only exists in the phase diagram for finite values of μ . For symmetric copolymers ($f = 1/2$) the parameter μ vanishes, and only the lamellar phase is predicted to form in the bulk, at $\alpha = 0$.

The Landau-Ginzburg free energy (1) can also be used to construct the interfacial free-energy excess $\bar{\Omega}$ for systems where the translational invariance has been broken by the presence of an interface:

$$\bar{\Omega} = \int_V dV [\psi(\mathbf{r}) U(\mathbf{r}) + F[\psi(\mathbf{r})] - F[\psi(x,y,z \rightarrow \infty)]] \quad (10)$$

In this equation U is the surface potential. For a contact potential it can be written as $U(z) = -\Delta\gamma\delta(z)$, where $\Delta\gamma$ is the differential affinity of the interface with respect to polymer A. If γ_{AS} and γ_{BS} are the interfacial tensions of polymers A and B with respect to the surface, one has $\Delta\gamma = \gamma_{BS} - \gamma_{AS}$. In order to obtain a tractable expression for the excess free energy, we first remark that for a weak enough hexagonal-lamellar transition (which implies a weak enough third coefficient μ or equivalently f close enough to $1/2$) the bulk correlation length can still be large compared to q_0^{-1} , the period of the ordered phases. In this limit we look for solutions of the order parameter $\psi(z, y)$ as in eq 3 but with z -dependent amplitudes. The symmetry of our problem, where the interface is taken to lie in the $[x, y]$ plane, implies that only two out of the three amplitudes are independent, $a_1(z) \neq a_2(z) = a_3(z)$. The slow variation of the amplitudes on the scale of the crystalline wavelength allows us to make a gradient expansion. We first transform the structure factor (2) in the equivalent gradient operator of the real space, then

insert the solutions for the order parameter with z -dependent amplitudes, and eventually coarse-grain the functional free energy on scales smaller than q_0^{-1} , keeping only gradients up to the square terms. This leads to the following equivalent excess free energy per unit surface, where the x and y variables have been integrated out:

$$\Omega = -\frac{8}{3}\Delta\gamma a_1(z=0) + \int_0^\infty dz \left[4cq_0^2 \left[\left(\frac{\partial a_1}{\partial z} \right)^2 + 2 \left(\frac{\partial a_2}{\partial z} \right)^2 \right] + F_{lh}[a_1(z), a_2(z)] - F_{lh}[a_1(\infty), a_2(\infty)] \right] \quad (11)$$

where the bulk density F_{lh} is the mixed function (eq 4, with $a_2 = a_3$)

$$F_{lh} = \tau(a_1^2 + 2a_2^2) - 2\mu a_1 a_2^2 + \frac{\lambda}{4}(a_1^4 + 6a_2^4 + 8a_1^2 a_2^2) \quad (12)$$

This expression gives the hexagonal free-energy density in the bulk when $a_1(\infty) = a_2(\infty)$ and the lamellar energy density whenever $a_2 = 0$.

A crucial point to remember is that only the amplitude a_1 is coupled to (and thus enhanced by) the surface potential. It is this coupling that leads to a lamellarlike interfacial phase where a_1 is large and a_2 and a_3 are small. The interfacial profiles can be obtained by functional minimization of the excess free-energy (eq 11) with respect to the amplitudes a_1 and a_2 . Renormalizing the distances by $z = t\xi$ with $\xi^2 = 8cq_0^2\lambda/\mu^2$, and the amplitudes as in the bulk case, one gets the new surface excess functional

$$\Omega \frac{\lambda^3}{\mu^4 \xi} = -CX(t=0) + \int_0^\infty dt \left[\frac{1}{2} \left(\frac{\partial X}{\partial t} \right)^2 + \left(\frac{\partial Y}{\partial t} \right)^2 + \bar{F}_{lh}[X(t), Y(t)] - \bar{F}_{lh}[X(\infty), Y(\infty)] \right] \quad (13)$$

with $\bar{F}_{lh}[X, Y] = \alpha(X^2 + 2Y^2) - 2XY^2 + 1/4(X^4 + 6Y^4 + 8X^2Y^2)$ and where C is given by $C = 8\Delta\gamma\lambda^2/(3\xi\mu^3)$. Minimizing (13) with respect to X and Y , one gets the following two coupled differential equations

$$\begin{aligned} \frac{d^2X}{dt^2} &= (-2\alpha + 4Y^2)X + X^3 - 2Y^2 \\ \frac{d^2Y}{dt^2} &= (-2\alpha - 2X + 2X^2)Y + 3Y^3 \end{aligned} \quad (14)$$

which are to be solved subject to the boundary conditions

$$\begin{aligned} \frac{dX}{dt}(t=0) &= -C \\ \frac{dY}{dt}(t=0) &= 0 \\ X(t=\infty) = Y(t=\infty) &= \frac{1 + (1 + 10\alpha)^{1/2}}{5} \end{aligned} \quad (15)$$

There is an interesting analogy between our copolymer system and the movement of a classical particle of mass unity moving in the $[X, Y]$ space under the potential $-F_{lh}(X, Y)$.¹³ The solutions of the amplitude equations (14) correspond to the trajectory of a particle starting at a special point in the $[X, Y]$ plane with a speed $-C$ parallel to the X -axis and terminating at $[X_\infty, Y_\infty]$ with zero speed. The positions in the classical potential corresponding to the pure lamellar or hexagonal phases are tops of hills; see Figure 2. Above the transition temperature between the hexagonal and lamellar phases the hexagonal hill is higher than the lamellar one. At the transition temperature the

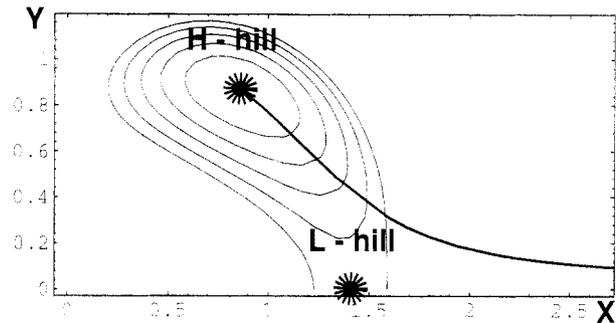


Figure 2. Trajectory of a classical particle in the mixed potential (eq 12), far from the hexagonal-lamellar phase transition ($\alpha = 1$). The reduced surface strength is $C = 10$. The point where the trajectory stops is the top of the hexagonal hill. The lamellar metastable point in this $[X, Y]$ space is at $[\sqrt{2}, 0]$. Drawn equipotential lines are at levels $-0.1, -0.2, -0.3, -0.4$, and -0.5 .

two hills have the same height. Because there is conservation of the total energy, it is possible to define the curve in the $[X, Y]$ space where the initial point must be located (complete determination of the initial position would require a second integral of motion or the resolution of the differential equations of motion (eq 14)). For our boundary conditions this curve is simply the equipotential line at the level $-C^2/2$ from the top of the hexagonal hill.

As can be seen from Figure 2, above the transition temperature, only a small closed line around the top of the H -hill is available as a starting point. This corresponds to small differential affinities of the surface with respect to monomers A and B, well above the transition temperature, where the interfacial structure only deviates slightly from the bulk phase. Linearization of the trajectory equations is possible in this case, leading to the solutions

$$\begin{aligned} \Delta X &= X - X_\infty = \frac{C}{3k_1} \exp\{-k_1 t\} + \frac{2C}{3k_2} \exp\{-k_2 t\} \\ \Delta Y &= Y - Y_\infty = \frac{C}{3k_1} \exp\{-k_1 t\} - \frac{C}{3k_2} \exp\{-k_2 t\} \end{aligned} \quad (16)$$

with k_1 and k_2 given by $k_1^2 = -2\alpha - 4X_\infty + 15X_\infty^2$ and $k_2^2 = -2\alpha + 2X_\infty + 3X_\infty^2$.

If one increases the adsorption strength C at fixed temperature (or decreases the temperature at fixed C), the line of possible starting points crosses the $Y = 0$ axis, leading to a possible solution for the trajectory where the phase at the interface would be purely lamellar. However, it is clear from the equations of motion (eq 14) that a particle starting at $Y = 0$ with $dY/dt = 0$ would never reach the top of the hexagonal hill at $t = \infty$. A small hexagonal component must thus always exist at the interface. We present in Figures 3-7 two profiles obtained by numerical integration of the differential equations describing the trajectory and the corresponding interfacial structure of the hexagonal phase. The first profile was obtained at temperatures far from the transition temperature. In this case the trajectory never gets close to the L -hill top, and the profiles go monotonically toward their bulk equilibrium values. Note also that in this case the curvature of the enhanced X amplitude never changes sign.

The second profile was obtained close to the transition temperature α_c . In order to understand the foot in the profile, we need to follow the trajectories for temperatures close to α_c . Immediately below α_c the particles need to stop at the top of the L -hill because the bulk equilibrium phase is then the lamellar phase. At the transition temperature α_c there is, somewhere in the bulk, a free

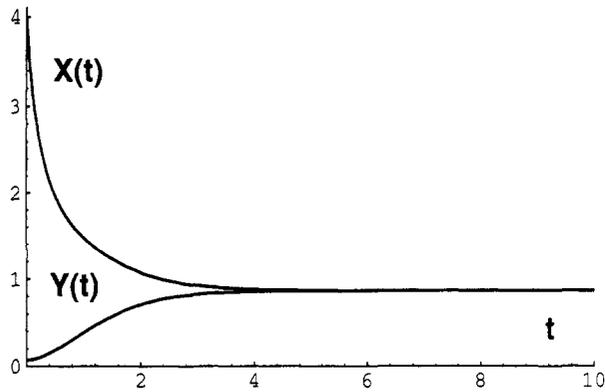


Figure 3. Time dependence of the amplitude profiles corresponding to the trajectory in Figure 2. The curvature of the enhanced X amplitude never changes sign.

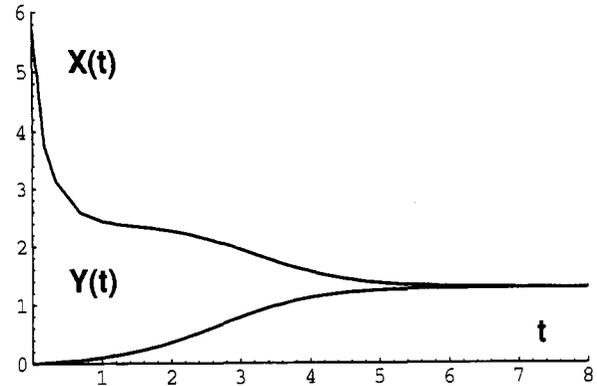


Figure 6. Time dependence of the amplitude profiles corresponding to the trajectory in Figure 5. The point where the curvature of the enhanced X-amplitude changes sign defines the half-thickness of the layer.

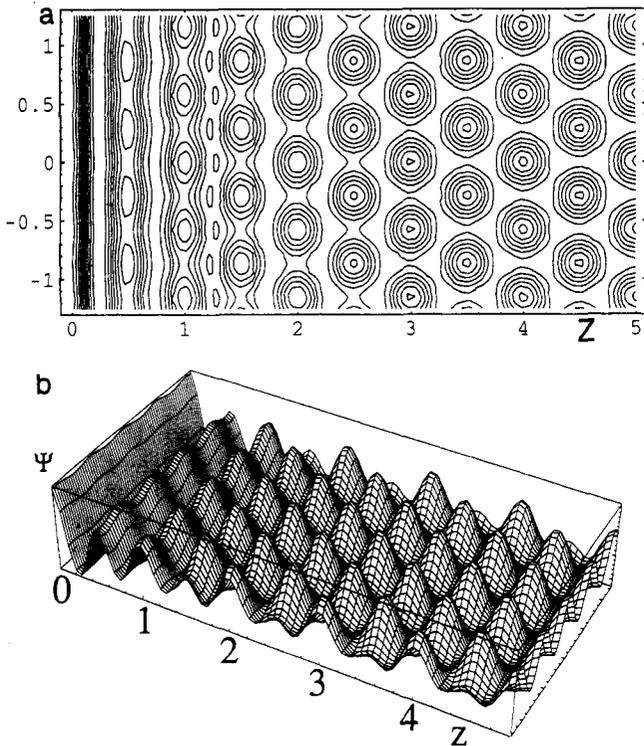


Figure 4. (a) Contour plot of the interfacial region of the hexagonal phase with the amplitude profiles of Figure 3. The correlation distance ξ defined in the text is taken in this case to be equal to $4\pi q_0^{-1}$. (b) Three-dimensional plot of the same interfacial region.

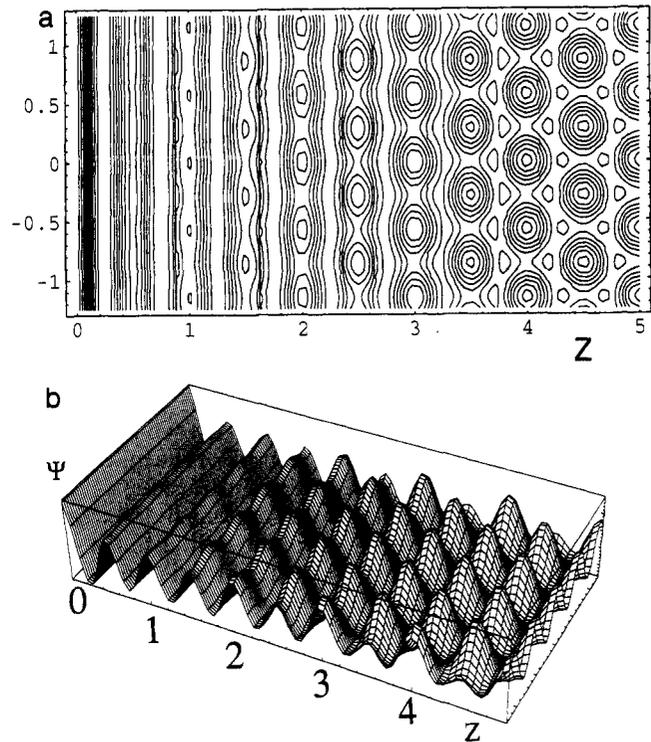


Figure 7. (a) Contour plot of the interfacial region of the hexagonal phase with the amplitude profiles of Figure 6. The correlation distance ξ defined in the text is taken in this case to be equal to $4\pi q_0^{-1}$. (b) Three-dimensional plot of the same interfacial region.

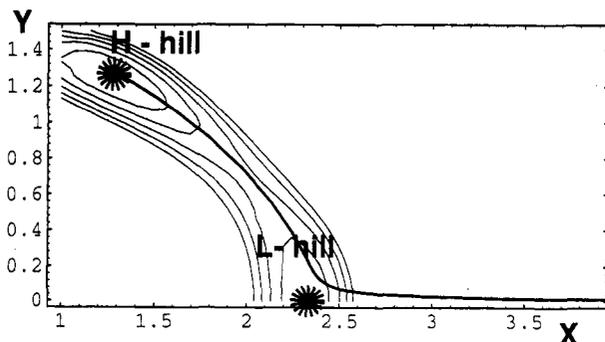


Figure 5. Trajectory of a classical particle in the mixed potential (12), close to the hexagonal-lamellar phase transition ($\alpha = 2.8$). The reduced surface strength is $C = 20$. The point where the trajectory stops is the top of the hexagonal hill. The lamellar metastable point in this $[X, Y]$ space is at $[5.6^{1/2}, 0]$. Drawn equipotential lines are at levels $-0.1, -0.2, -0.3, -0.4$, and -0.5 . interface between the lamellar and hexagonal phases. For temperatures approaching the transition temperature from above, the trajectories pass increasingly closer to the top

of the lamellar hill where they have a small speed; see Figure 5. This slowing down shows up in the profile as a foot which extends up to a distance l which diverges logarithmically with $\alpha - \alpha_c$

$$l = aR \log\{b(\alpha - \alpha_c)\} \quad (17)$$

where a and b are functions of the surface strength $\Delta\gamma$. This logarithmic divergence can be understood as follows: Let r be a variable defined from $dr^2 = dX^2 + 2dY^2$; the trajectories will then be parametric functions of the variable r which runs from r_s at the surface to r_∞ in the bulk. In $[X, Y]$ space there is a point $[X(r^*), Y(r^*)]$, close to L , where R has a maximum in r and where the profile $r(z)$, given by $dz = dr/[F_{hl}(r)]^{1/2}$, also slows down and exhibits a foot. If we expand the free energy around r^* and define l as the distance along z which separates r_s from r^* , one gets the characteristic logarithmic divergence of eq 17, often found in wetting problems.¹⁴

Summarizing the results for the weak segregation case, we stress the following:

(1) The lamellar order appearing close to the interface of a weak hexagonal phase of diblock copolymers is induced by the preferential coupling between the surface potential and the wave component perpendicular to the interface.

(2) The extent of the lamellar region diverges logarithmically with the relative decrease in temperature below the lamellar-hexagonal transition.

The formalism developed in this section bears strong similarities with the work of Frederickson⁵ on the interfacial behavior of symmetric diblock copolymers, and the main results of ref 5 may be recovered in the limit of $\mu \rightarrow 0$. Two main differences are to be noted however. First, our treatment of the interfacial inhomogeneities is based on the gradient expansion of the free energy, instead of the mixed gradient/Green function representation for the real space form of the scattering function $S(q)$. Second, we neglected all the details related to the definition of the exact phase matching of the bulk phase with the interface; we rather assume the wave phase to be such that the composition which couples strongly with the interface has its maximum there. A better phase matching can in principle be achieved by introducing an arbitrary phase φ in the definition of the hexagonal wave composition (eq 3) and then fixing it by the conservation condition $\int \psi dz = 0$.

Surface potentials with two parameters have also been considered by Hauge,¹⁵ who studied the mean-field wetting behavior of a three-state Potts model. In wetting more refined versions of the surface contribution to the free energy are often used. In particular, one introduces a phenomenological second virial coefficient (the coefficient of the second-order term in an expansion of the surface energy in powers of ψ_s) which describes the relative change induced by the surface on the strength of the microscopic interactions. If such a term is taken into account, the line of possible starting points for the particle in the classical analogy is no longer an equipotential line but a curve generated by the intersection of the potential surface and an inclined plane. Obviously we have not attempted here a general description of the wetting phenomena generated by this additional parameter, but rather supposed that the main effect is driven by $\Delta\gamma$, the surface chemical potential which corresponds in our case to the difference in interfacial tensions between each of the blocks and the surface. It is worth noting that, according to the classification of Hauge, our Landau's free-energy density falls in the case where the wetting transition, when it exists, is first order.

III. Strong Segregation

Our treatment of the interfacial structure of a strongly segregated hexagonal phase proceeds as follows. We first assume that there exists a surface layer of lamellar ordering, with thickness ξ , and that the lamellar phase matches onto the hexagonal phase at some interface. At this interface the incompressibility of the melt forces the lamellae to undulate so as to physically match the contour of the hexagonal phase; see Figure 8. The lamellar layer nearest the surface is flat, and the undulation in the lamellar layers grows monotonically as one travels from the flat surface to the interface with the hexagonal region. The bending and compressional moduli of the lamellar layer tend to suppress rapid growth of undulations near the flat surface. We will model the mechanical properties of the lamellar phase using these bending and compressional terms in a derivative expansion of the free energy. One might expect there also to be some distortion in the hexagonal region, close to the interface with the lamellar phase, although we neglect this here. We expect this simplification to have

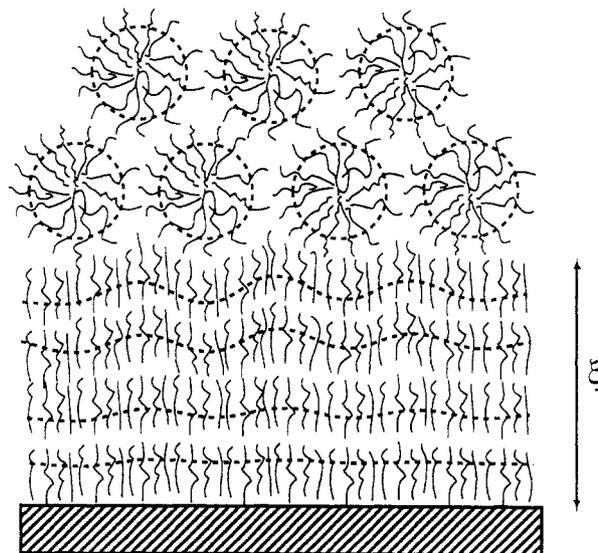


Figure 8. Schematic diagram of the lamellar ordering induced by a solid surface and the undulation which develops to match onto the hexagonal phase at the hexagonal/lamellar interface. We see a slice through the y - z plane with symmetry in the x -direction. The dotted circles represent the position of the interfaces between the A and B blocks of the copolymers.

little effect on our results, at least at the qualitative level of interest in the present work.

Since the bulk phase is hexagonal, there is a free-energy difference (per unit volume) ΔF between the hexagonal and lamellar phases which suppresses the extent of any lamellar region. The extent of this region is also suppressed by the bending and compressional energies of the lamellar phase. Balancing these energetic penalties is the difference in surface tension between the two chemical components at the surface $\Delta\gamma$ which is what drives the lamellar ordering: the lamellar phase allows the component which minimizes the surface tension to concentrate at the surface, while the symmetry of the hexagonal phase requires both A and B components to reside there, with an associated energetic penalty.

While this treatment is formulated in the limit of a completely inflexible (solid) surface, a copolymer/air interface (say) results in a surface which is approximately flat provided the surface tension between the copolymer and the air is sufficiently large.¹⁶ The necessary condition is $\gamma/(KB)^{1/2} \gg 1$, where γ is the copolymer/air surface tension and K and B are the bending and compressional moduli of the lamellar phase, respectively. Recent experiments on the PS/PBMA system¹⁷ suggest that $\gamma/(KB)^{1/2} \approx 27$, leading to a rather flat surface.

III.1. Smectic Energy. We consider a system comprising an infinite, flat solid surface in contact with a strongly segregated diblock copolymer melt in which the bulk stable phase is hexagonal. We take the normal to the solid surface to define the z -direction and the axis of symmetry of the hexagonal phase to define the x -direction. We assume that a region of lamellar ordering exists in the vicinity of the surface; see Figure 8. The local vertical displacement of the lamellar layer is u , and we take the continuum limit where u varies smoothly throughout the sample. We take the following as the energy density of the lamellar phase^{18,19} (per unit length in the x -direction):

$$F = \frac{B}{2} \left(\frac{\partial u}{\partial z} \right)^2 + \frac{K}{2} \left(\frac{\partial^2 u}{\partial y^2} \right)^2 \quad (18)$$

Here K is the bending or splay modulus and B is the compression modulus. This expression includes only the leading order terms in an expansion of the energy density

in derivatives of u and is therefore only strictly valid provided u is slowly varying.

We retain only the first Fourier component of the lamellar displacement field $a(z)$ with $u = a(z) \cos qy$. Using eq 18 the free-energy density of the lamellar phase becomes

$$F(z) = \frac{B}{4} \left(\frac{da}{dz} \right)^2 + \frac{Kq^4}{4} a^2 \quad (19)$$

The boundary conditions are that the amplitude of the deformation vanishes at the solid surface $a(0) = 0$ and that the undulation of the lamellae must match onto the hexagonal phase at the relevant interface, approximated by $a(\xi) = a_0$. Minimizing eq 19, we find that a is given by

$$a(z) = a_0 \frac{\sinh \nu z}{\sinh \nu \xi} \quad (20)$$

with ν a characteristic inverse length given by $\nu = q^2(K/B)^{1/2}$. Substituting eq 20 into eq 19 and integrating over $0 < z < \xi$, we obtain the smectic free energy per unit area F_A

$$F_A = \frac{1}{4} a_0^2 (KB)^{1/2} q^2 \coth \nu \xi \quad (21)$$

In order to determine the penetration depth ξ , we consider the free energy per unit area F , which includes the free-energy difference (per unit volume) between the hexagonal and the lamellar phases ΔF :

$$F = F_A(\xi) + \Delta F \xi \quad (22)$$

Minimizing F with respect to ξ , we find that ξ is given by

$$\xi = \frac{1}{\nu} \sinh^{-1} \left(\frac{K a_0^2 q^4}{4 \Delta F} \right)^{1/2} \quad (23)$$

which simplifies in both the limits of large and small ξ to

$$\xi = \begin{cases} \frac{1}{2\nu} \log(K a_0^2 q^4 / \Delta F) & \text{for } \xi \nu \gg 1 \\ \frac{1}{2\nu} (K a_0^2 q^4 / \Delta F)^{1/2} & \text{for } \xi \nu \ll 1 \end{cases} \quad (24)$$

As we shall see below the product $\xi \nu$ corresponds to the number of lamellar layers present, to within a numerical factor of order unity. Hence, the limit $\xi \nu \ll 1$ may have little physical significance.

Recent theoretical work on diblock copolymer lamellae has provided a microscopic calculation of the smectic moduli for a symmetric $f = 1/2$ lamellar layer.²⁰ These are $B = 3\gamma_{AB}/h$ and $K = \gamma_{AB}h/3$ where $h = (\gamma_{AB}/3)^{1/3} N^{2/3}$ is the thickness of a single lamellar layer and γ_{AB} is the surface tension which acts at the interface between the A and B blocks in a lamellar layer. This in turn has been calculated by Semenov⁴ for very long chains and is well approximated by $\gamma_{AB} \approx b\chi^{1/2}$ where b is the monomer size. Assuming that the smectic moduli do not depend crucially on f , we may use the above expression as estimates whenever $f \neq 1/2$. The amplitude and the wavelength of the lamellar undulations are both of the order of the hexagonal lattice size (repeat distance) which is itself of the order of the lamellar thickness h . Thus, recalling the definition of $\nu = q^2(K/B)^{1/2}$, the product $\xi \nu$ can be identified with the number of layers in the lamellar region to within a numerical prefactor of order unity. Using these estimates, eq 24 with $\xi \nu \gg 1$, and neglecting numerical factors of order unity, we find

$$\xi/h \approx \text{const} + \log \frac{\gamma_{AB}}{h \Delta F} \quad (25)$$

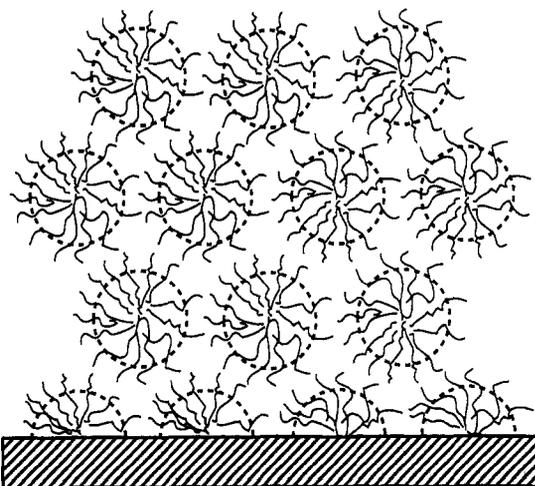


Figure 9. Schematic diagram of the polymer conformations for the case when no region of lamellar ordering exists. We see a slice through the y - z plane with symmetry in the x -direction. The dotted circles represent the position of the interfaces between the A and B blocks of the copolymers. Note that both the A and B components of the copolymer are in contact with the surface.

This behavior, where ξ diverges logarithmically as $\Delta F \rightarrow 0$, suggests that ξ is rarely very large. An estimate of ΔF may be obtained from the theory of ref 4. One simply compares the free-energy densities of the hexagonal and lamellar phases near the phase boundary, expanding to first order in f .

$$\Delta F = \text{const} (\gamma_{AB}/N)^{2/3} (f_0 - f) \quad (26)$$

where $f_0 \approx 0.28$ is the position of the phase boundary and the constant of proportionality has a numerical value of approximately 3.05.

Three main approximations are inherent in the preceding treatment: (i) We ignore the effect of any distortion to the hexagonal phase near the interface with the lamellar region. (ii) We neglect all higher order Fourier components of the displacement field u . (iii) We utilize an expansion of the free energy equation 18 which is strictly only valid for slowly varying perturbations. However, we do expect our results to remain accurate at the qualitative level.

III.2. Overall Stability of the Lamellar Region. Even in copolymer melts where the bulk phase is hexagonal, the difference in surface tension between the A and B components at a surface $\Delta\gamma$ may stabilize a region of lamellar ordering at that surface; compare Figures 8 and 9. This is because the lamellar phase allows the component which minimizes the surface tension to reside at the surface while the symmetry of the hexagonal phase requires both A and B components to be in contact with it, with an associated energetic penalty; see Figure 9. A lamellar region will exist provided $\Delta\gamma$ is large enough to overcome the sum of the free-energy penalty for creation of the lamellar region and the bending and compressional energies of the deformed lamellar layers.

Hence the lamellar region exists whenever the energy difference $\Delta\Omega$ is negative

$$\Delta\Omega = F_A(\xi) + \Delta F \xi - p \Delta\gamma \quad (27)$$

where $p(f) \sim 1$ is the proportion of the surface which would be in contact with the unfavorable polymer component if the hexagonal phase existed at the surface; see Figure 9. Solving $\Delta\Omega = 0$ for $\Delta\gamma$ determines the smallest value of $\Delta\gamma$, written $\Delta\gamma_c$, for which the lamellar region exists. Using the above estimates $K \approx \gamma_{AB}h$, $B \approx \gamma_{AB}/h$, $q \approx 1/h$, and $a_0 \approx h$, and solving for $\Delta\gamma_c$ in the limit $\xi \nu \gg 1$, we find

$$\Delta\gamma_c \simeq \gamma_{AB} \quad (28)$$

where we have neglected all prefactors of order unity. Equation 28 suggests that $\Delta\gamma_c$ is comparable to the surface tension between the two chemical components of the copolymer. Since the surface tensions at a polymer/air interface (say) can be much larger than γ_{AB} , it seems likely that the condition $\Delta\gamma > \Delta\gamma_c$ may be readily accessible experimentally.^{16,17}

IV. Discussion and Conclusions

In the present work we have studied the surface-induced lamellar ordering which may occur in a bulk hexagonal phase of block copolymers. The surface, which is treated as flat, may either be a solid surface or a copolymer/air interface provided the surface tension is large enough to result in a nearly flat surface.^{16,17} Some experimental evidence for the existence of surface-induced lamellar ordering has been reported, for instance, in refs 21–23. In a more recent work,²⁴ Liu *et al.* make a detailed analysis of the interfacial structure of asymmetric diblock and triblock copolymers of deuterated polystyrene and poly(vinylpyridine). For the samples which order parallel to the silicon oxide substrate, the first layer is shown to be of pure lamellar morphology, in agreement with the general picture developed above.

In the weak segregation limit, with the block copolymer just below the order–disorder transition temperature T_{ODT} , the system was modeled using a Landau–Ginzburg expansion. We found that lamellar ordering can appear close to the surface of a weakly hexagonal phase of diblock copolymers. This lamellar ordering is induced by the preferential coupling between the surface potential and the wave component perpendicular to the interface. It was also found that the extent of the lamellar region diverges logarithmically with temperature below the lamellar–hexagonal transition.

As mentioned before, at the level of the mean-field description for the order–disorder transition the characteristic wavevector q_0 is taken as a constant. It was, however, shown by neutron scattering experiments²⁵ and numerical simulations²⁶ that the peak position of the fluctuation spectrum varies throughout the transition region. This effect has been theoretically explained^{27,28} by taking into account the role of fluctuations on the phase transition and relaxing the constraint on the value of the wave vector. It is interesting to remark that treatment of this effect in our framework can potentially lead to a z -dependent value of the period of the interfacial structures, in addition to the amplitude modulation that we describe in our paper.

In the strong segregation regime, well below T_{ODT} , we have employed the classical theory of smectic liquid crystals. We determine a lower critical value for the surface tension difference between the A and B polymers and the surface $\Delta\gamma_c$, which is found to be of the order of the surface tension γ_{AB} which acts at the interface between the A and B blocks: only for surface tension differences above this value will a region of surface-induced lamellar ordering occur. Such surface tensions may well be readily accessible to experiments. We also found that the penetration depth ξ of the lamellar ordering induced at the surface depends on the chemical potential difference between the hexagonal and lamellar phases ΔF and diverges like $|\log \Delta F|$ for $\Delta F \rightarrow 0$. The logarithmic behavior, found in both the weak

and strong segregation regimes, suggests that ξ is rarely very large. This is consistent with the presence of a single layer in the system of ref 24. A larger number of layers would require values for the copolymer asymmetry much closer to the values at which the lamellar phase forms in the bulk.

While the possibility of a similar region of induced lamellar ordering in other regions of the phase diagram (e.g., where the equilibrium phase is cubic) was not explicitly considered, we are able to make some general observations. In both the weak and strong segregation regimes the calculations are expected to be very similar to those presented here. In the strong segregation regime there is only a different boundary condition on the deformation of the lamellar layers at the lamellar/cubic interface, while in the weak segregation regime a slightly different Fourier expansion in the local concentration difference is required. Hence, we expect results similar to those obtained for the case of a hexagonal phase. However, in the strong segregation regime the chemical potential difference between the cubic and lamellar phases will never be very small, and the extent of the lamellar region is expected to be severely limited.

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