1. 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 of layers (the lamellar phase), rods (the hexagonal phase), spheres (the cubic phase) as well as others[2]. In the so-called weak segregation limit the excess of one of the species varies smoothly over the sample whilst in the strong segregation limit $T \ll T_{ODT}$ there is a sharp interface between alternate regions of almost pure A or B blocks.

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 behaviour is sensitive to two parameters[3,4] (i) χN, where χ is the Flory incompatibility parameter between polymer A and B, in $k_B T$ units, and (ii) the molecular asymmetry parameter $f \equiv N_A/N$. For symmetric ($f = 1/2$) copolymers the lamellar phase is formed[3] for temperatures $\chi N > 10.49$. 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 phase behaviour is mainly controlled by f. The hexagonal phase is found for $0.12 < f < 0.28$ whereas the lamellar and cubic phases are found for $0.28 < f < 0.5$ and $f < 0.12$ respectively[4]. 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.

II. Weak Segregation

We study the interfacial structure 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 content of (say) monomers A, $\psi(\mathbf{r}) = \phi_A(\mathbf{r}) - \langle \phi_A \rangle$

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

(1)

where $S(q = |\mathbf{q}|)$ is the Fourier transform of the two-point correlation function in the disordered homogeneous phase, and ψ_q the $q-$Fourier component of the order parameter ψ. Close to the order-disorder transition the susceptibility $S(q)$ is strongly peaked around some vector q_0 and can be approximated by $S^{-1}(q) = \tau + c\,(q^2 - q_0^2)^2$ with an effective temperature $\tau = 2(\chi N)_s - 2(\chi N)$.

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

$$\psi(z, y) = 2a_1 \cos\{q_0 z\} + 2a_2 \cos\{q_0 \frac{\sqrt{3}y - z}{2}\} + 2a_3 \cos\{-q_0 \frac{\sqrt{3}y + z}{2}\} \qquad (2)$$

with $a_1=a_2=a_3=a_h$. Whilst instead the lamellar phase corresponds to $a_1=a_l$ and $a_2=a_3=0$.

The interfacial free-energy excess $\bar{\Omega}$ near an interface is given by

$$\bar{\Omega} = \int_V dV \left[\psi(\mathbf{r})U(\mathbf{r}) + F[\psi(\mathbf{r})] - F[\psi(x,y,z \to \infty)] \right] \qquad (3)$$

Here U is the surface potential, for which we employ $U(z) = -\Delta\gamma\delta(z)$, where $\Delta\gamma = \gamma_{BS} - \gamma_{AS}$ and γ_{AS} and γ_{BS} are the interfacial tensions of polymers A and B with respect to the surface. For a weak enough hexagonal-lamellar transition (which implies a weak enough asymmetry μ) 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 (2) but with z−dependent amplitudes. By symmetry 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 renormalise the distances by $z = t\xi$ with $\xi^2 = 8cq_0^2\lambda/\mu^2$, and the amplitudes by $a_2 = Y\mu/\lambda$ and $a_1 = X\mu/\lambda$, where the bulk equilibrium values of the amplitudes are $X = \sqrt{2\alpha}$ and $Y = \frac{1+\sqrt{1+10\alpha}}{5}$ with $\tau = -\alpha\mu^2/\lambda$. Integrating and minimising with respect to X and Y we obtain the following two coupled differential equations

$$\frac{d^2X}{dt^2} = \left(-2\alpha + 4Y^2\right) X + X^3 - 2Y^2$$
$$\frac{d^2Y}{dt^2} = \left(-2\alpha - 2X + 2X^2\right) Y + 3Y^3 \qquad (4)$$

where $C = 8\Delta\gamma\xi\lambda^2/(3\mu^3)$. These are to be solved subject to the boundary conditions $\frac{dX}{dt}(z = 0) = -C$, $\frac{dY}{dt}(z = 0) = 0$ and $X(t = \infty) = Y(t = \infty) = \frac{1+\sqrt{1+10\alpha}}{5}$ There is an interesting analogy between our copolymer system and the movement of a classical particle of mass unity moving in (X, Y) space. The solution of (4) corresponds to the trajectory of a particle starting with a speed $-C$ tangential to the X−axis and terminating at (X_∞, Y_∞) with zero speed, see Fig. 1a. The positions corresponding to the pure lamellar or hexagonal phases are tops of hills. Above the transition temperature between the hexagonal and lamellar phases the height of the hexagonal hill is larger then the height of the lamellar hill. 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). This curve is simply the equipotential line at the level $-C^2/2$ from the top of the hexagonal hill.

In Fig. 1a we present a trajectory obtained by numerical integration of the differential equations (4) describing the interfacial structure. 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. This slowing down, and hence the region of lamellar-like ordering, extends up to a distance l which diverges logarithmically with the distance from the transition tempreature in α units, $\alpha - \alpha_c$ ($\alpha_c = (7 + 3\sqrt{6})/5 \approx 2.87$)

$$l = aR\log\{bN(\alpha - \alpha_c)\} \tag{5}$$

where a and b are functions of the surface strength $\Delta\gamma$. The logarithmic divergence is characteristic of wetting problems.

(a)   **(b)**
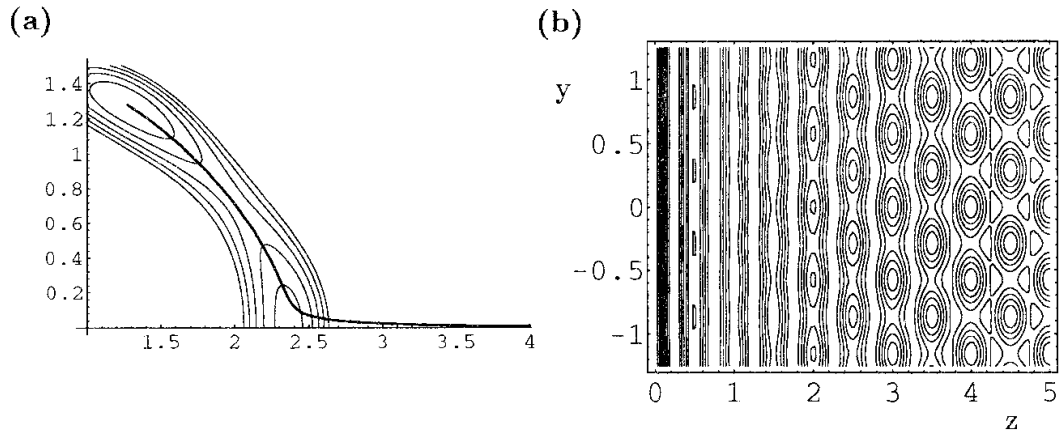
Figure 1 **(a)** The trajectory of a classical particle according to the "equations of motion" (4), close to the hexagonal-lamellar phase transition ($\alpha = 2.8$, $\alpha - \alpha_c = -0.07$). The reduced surface strength is $C = 20$. The trajectory stops at the top of the hexagonal hill at $t, z \to \infty$. The lamellar metastable point is at $(\sqrt{5.6}, 0)$. Drawn equipotential lines are at levels -0.1, -0.2, -0.3, -0.4, -0.5. **(b)** A contour plot of ψ in the same interfacial region. The correlation distance ξ defined in the text is taken in this case to be equal to $4\pi q_0^{-1}$.

Summarizing the results for the weak segregation case we stress that: (i) The lamellar order appearing close to the surface in our weakly ordered hexagonal phase is induced by the preferential coupling between the surface potential and the wave component perpendicular to the interface. (ii) The extent of the lamellar region diverges logarithmically with the relative decrease in temperature below the lamellar - hexagonal transition.

III. Strong segregation

We assume that a region of lamellar ordering exists in the vicinity of the

surface, see Fig. 2. The normal to the solid surface and the axis of symmetry of the hexagonal phase define the z- and x-directions respectively. The local vertical displacement of the lamellar layer is u and we take the continuum limit where u varies smoothly throughout the sample. The energy density of the deformation of the lamellar phase, for $z < \xi$, is[5]

$$F = \frac{B}{2}\left(\frac{\partial u}{\partial z}\right)^2 + \frac{K}{2}\left(\frac{\partial^2 u}{\partial y^2}\right)^2 \tag{6}$$

Here K is the bending or splay modulus and B is the compression modulus.
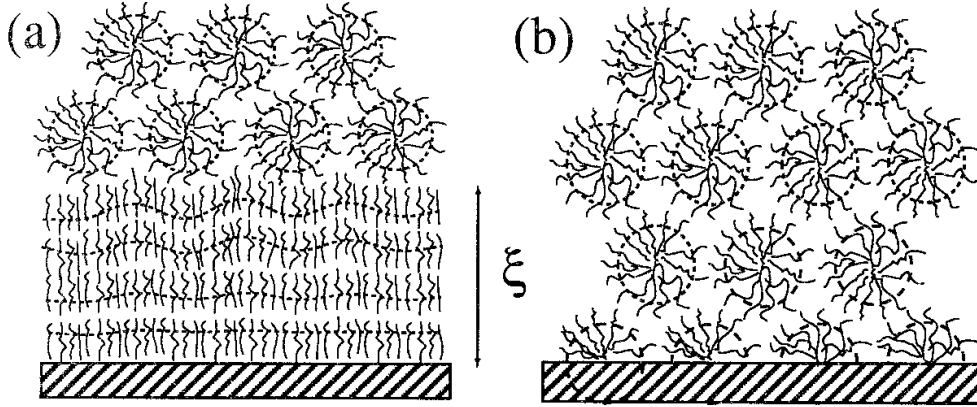
Figure 2 (a) Schematic diagram of the lamellar ordering which may be induced at the surface. We see a slice through the y-z plane with symmetry in the x-direction. The dotted circles represent the position of the interfaces between the A and the B-blocks of the copolymers. (b) The alternative case that no lamellar ordering exists. Note that both A and B components of the copolymer are in contact with the surface in this case.

We retain only the first fourier component of the lamellar displacement field $a(z)$ with $u = a(z)\cos qy$. The boundary conditions are that the solid surface is flat $a(0) = 0$ and that the undulation of the lamellae must match onto the hexagonal phase at the relevant interface, approximated by $a(\xi) = a_o$. Minimising (6) we find that $a(z) = a_o\frac{\sinh\nu z}{\sinh\nu\xi}$ with ν a characteristic inverse length given by $\nu = q^2\sqrt{K/B}$. By using this result for $a(z)$, integrating over $0 < z < \xi$ and adding the surface and chemical potential contributions we obtain the total free energy excess per unit area

$$\Delta\Omega = \frac{1}{4}a_o^2\sqrt{KB}q^2\coth\nu\xi + \Delta F\,\xi - p\Delta\gamma \tag{7}$$

where ΔF is the chemical potential between the hexagonal and lamellar phases and $p(f) \sim 1$ is the proportion of the surface which would be in contact with the unfavourable polymer component if the hexagonal phase existed at the surface, see Fig. 2b. In order to determine the penetration depth ξ we minimise $\Delta\Omega$ with respect to ξ

$$\xi = \frac{1}{\nu}\sinh^{-1}\left(\frac{K\,a_o^2 q^4}{4\Delta F}\right)^{1/2} \tag{8}$$

Which simplifies in the limit $\xi\nu \gg 1$ (many layers) to $\xi = \frac{1}{2\nu}\log\left(K\, a_o^2 q^4/\Delta F\right)$.

We estimate[6] $B = 3\gamma_{AB}/h$ 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 $\gamma_{AB} = b\chi^{1/2}$, where b is the monomer size, is the interfacial tension acting at the AB interface[4]. The amplitude and the wavelength of the lamellar undulations at the interface with the hexagonal phase are both of the order of the hexagonal lattice size (repeat distance) which is itself of the order of the lamellar thickness h. Thus the product $\xi\nu$ is the number of layers in the lamellar region, to within a numerical prefactor of order unity. Using these estimates and neglecting numerical factors of order unity, we find

$$\xi/h \simeq \text{const} + \log\frac{\gamma_{AB}}{h\Delta F} \qquad (9)$$

This behaviour, where ξ diverges logarithmically as $\Delta F \to 0$, suggests that ξ is rarely very large. An estimate of ΔF may be obtained by comparing the free energy densities of the hexagonal and lamellar phases near the phase boundary[4]. To first order in f we find $\Delta F = \text{const}.(\gamma_{AB}/N)^{2/3}(f_o - f)$ where $f_o \approx 0.28$ is the position of the phase boundary and the constant of proportionality has a numerical value of approximately 3.05.

The lamellar region exists whenever the energy difference $\Delta\Omega$ is negative. Solving $\Delta\Omega = 0$ for $\Delta\gamma$ we find that the lamellar region exists for $\Delta\gamma > \Delta\gamma_c$ where $\Delta\gamma_c \simeq \gamma_{AB}$ in the limit $\xi\nu \gg 1$. Since the magnitude of the surface tensions at a polymer/air interface can be much larger than γ_{AB} it seems likely that this condition may be readily accessible experimentally.

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 utilise an expansion of the free energy Eq. (6) which is strictly only valid for slowly varying perturbations. However, we do expect our results to remain accurate at the qualitative level.

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