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Diblock Copolymer Lamellae at Rough Surfaces

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ABSTRACT: We study theoretically the behavior of a diblock copolymer lamellar layer, in the melt, assembled at a substrate with a small-amplitude periodic roughness, characterized by a wavevector q. The polymer configurations are described using the Alexander–de Gennes model of polymer brushes. For a single lamella of thickness h, at small wavevectors ($qh < 1$), the profile of the free surface follows closely the roughness of the substrate. There exists a finite value of the wavevector q_c ($q_c h \approx 2.6$) at which the upper surface is *completely flat*. At larger wavevectors $q > q_c$, the undulation of the free surface has a sign opposite to that of the solid surface; the two surfaces of the lamella undulate out of phase. In the limit of infinite wavevector, the midplane of the lamella is flat and the deformations of the two surfaces are symmetric with respect to reflection about the midplane. We also consider thicker films where many lamellar layers form a stack next to the surface. We determine the smectic elasticity of the lamellar phase for small wavevectors. We then discuss the penetration of the undulation induced by the substrate into the lamellar stack. At low wavevector the penetration depth diverges as q^{-2}, as in usual smectics; it vanishes at the wavevector q_c and then increases with wavevector.

1. Introduction

Certain diblock copolymers are known to self-assemble spontaneously in the melt to form spatially extended two-dimensional lamellae.[1,2] Each lamellar layer consists of polymers which are partially stretched in the z direction (say) while the layer itself is liquid and retains translational symmetry in the x–y plane. The self-assembly is driven by the immiscibility of the two chemical components of the polymer, denoted A and B. By forming a lamellar 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 a "stack" is formed in which the layers pile up alternately, A–B B–A A–B etc. This phase is a macromolecular analogue of the smectic A phases of liquid crystals.

In this paper we will consider the simple case of a symmetric A–B diblock copolymer melt and study small, static spatial deformations to the lamellar order, such as those induced by a rough solid surface. Specifically we consider one lamella (and subsequently a lamellar stack) with a small sinusoidal deformation of wavevector $q = 2\pi/\lambda$ imposed at one surface; the other surface is free to relax, as are the internal polymer configurations. Our study is relevant to recent experiments where the structure of the surface of thin copolymer films in a lamellar phase has been investigated by interference and atomic force microscopy[3] as well as neutron reflectivity[4] and small-angle X-ray scattering.[5] The roughness of the solid substrate on which the film is deposited induces a roughness of the interface between the copolymer film and the air that can be measured by grazing incidence X-ray scattering. We discuss here how the undulations of the air interface follow those of the solid surface. For a bulk lamellar phase, our results also provide a direct molecular determination of the smectic elasticity.

Recent theoretical work has concentrated on describing the phase equilibria of asymmetric diblock copolymer systems[6] by employing an electrostatic analogy. This same method has recently been extended[7] to describe the deformation energy of a permanently grafted homopolymer brush. Our work generalizes this approach to copolymer layers where the grafting density is a thermodynamic variable.

Throughout this paper, we describe the preference of the system to avoid A–B contacts by the introduction of a surface tension γ_{AB} which acts at the A–B interface. Hence we assume that the number of A–B contacts varies linearly with the area of the A–B interface. Within this scheme it is the balance between the surface tension and the elastic stretching energy of the polymers which determines the equilibrium flat lamellar thickness.

We also use the simplifying approximation that each chain terminates at the lamellar surface, i.e., that the chain ends are all localized at the interface between neighboring lamellae; in studies of polymer brushes this is commonly known as the Alexander–de Gennes approximation.[8,9] While it is known that the density of chain ends can be strongly peaked close to the surface,[10] the chain ends are believed to be distributed throughout the layer. However, the Alexander–de Gennes approximation has been shown to yield the correct scaling laws for the free energy of a flat lamella, with an error in the numerical prefactors of order 20% or so,[6,7] and we expect our approach to yield qualitatively accurate results, at least in the low-q limit.

The paper is organized as follows. The next section presents a calculation of the excess free energy due to the undulations of a single lamella. This free energy allows the determination of the undulation of the upper surface when the undulation of the lower surface is imposed. Section 3 is devoted to the smectic elasticity of a lamellar stack and to the penetration of an undulation toward the bulk of a lamellar phase. The experimental problem of a copolymer film on a rough solid surface is briefly discussed in section 4, where we include the polymer/surface and polymer/air interactions. The last section gives a discussion of the results and presents some possible issues.

2. Deformation of a Single Lamella

Our model system consists of a melt of monodisperse polymer chains, each with degree of polymerization N and monomer volume v. The copolymer thus consists of two blocks of $N/2$ monomers each of a different chemical nature (denoted A and B). These polymers are assumed to self-assemble to form a uniform lamellar sheet.

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We focus first on a single, isolated lamellar sheet, with mean thickness h, extending to infinity in the x–y plane. A small sinusoidal deformation with amplitude ϵ_l ($\epsilon_l/h \ll 1$) and wavevector q parallel to the x axis is imposed at the lower surface; the upper surface is free to relax. The lamellar sheet retains translational symmetry in the y direction. The z coordinates of the lower and the upper lamellar surfaces are denoted by z_l and z_u, respectively.

$$z_l(x) = \epsilon_l \cos qx \tag{1a}$$

$$z_u(x) = h + \epsilon_u \cos qx \tag{1b}$$

The undulation of the upper surface ϵ_u is, as yet, unknown but also remains small ($\epsilon_u/h \ll 1$). The Alexander–de Gennes approximation involves the assumption that all chain ends lie at the lamella surfaces. Without loss of generality we take the A ends to lie at the lower surface and the B ends to lie at the upper surface.

Following Semenov[6] we describe the local polymer stretching through the vector field of the chain tensions $\mathbf{E}$.

$$\mathbf{E}(\mathbf{r}) = \mathrm{d}\mathbf{r}/\mathrm{d}s \tag{2}$$

where the chain expends ds monomers in stretching over the distance d$\mathbf{r}$. The two components of the tension are defined by $\mathbf{E} = E_x\hat{\mathbf{x}} + E_z\hat{\mathbf{z}}$ ($E_y = 0$ by symmetry).

If we now choose an oriented surface element d$\mathbf{S}$, the incompressibility of the copolymer melt[11] relates the local chain tension $\mathbf{E}$ to the number of chains passing through d$\mathbf{S}$, which we write as dQ.

$$\mathbf{E}\cdot\mathrm{d}\mathbf{S} = \upsilon\, \mathrm{d}Q \tag{3}$$

Thus the number of chains passing through a surface element increases linearly with the local polymer stretching at that surface element. The integration of (3) over a closed surface leads to

$$\int_V \nabla\cdot\mathbf{E}\, \mathrm{d}V = \upsilon \int_S \mathrm{d}Q \tag{4}$$

The number of chains dQ can be expressed as a function of the difference between the density of polymer A ends ρ_A and polymer B ends ρ_B. The difference $\rho = \rho_A - \rho_B$ is the density of "chain sources"; the right-hand side of (4) can be written as $\upsilon\int_V \rho\, \mathrm{d}V$ so that

$$\nabla\cdot\mathbf{E} = \upsilon\rho \tag{5}$$

In the lamella interior where, within the Alexander–de Gennes approximation, there are no chain ends this equation reduces to

$$\nabla\cdot\mathbf{E} = 0 \tag{6}$$

If we now know the tension of the chains, i.e., the field $\mathbf{E}$, we can determine the elastic free energy of the polymer chains in the lamellae. We assume throughout the present work that although the chains are strongly stretched, all polymers remain in the regime where the elastic restoring force is linear in extension. As a first approximation each monomer can be viewed as a simple spring with an elastic energy proportional to $\mathbf{E}^2$. The total free energy is the sum of the free energy of all the monomers. Since the monomer density is a constant in the melt ($=1/\upsilon$), the elastic free energy is proportional to the integral of $\mathbf{E}^2$ throughout the lamella interior. This is the great simplification offered by the Alexander–de Gennes approximation in which one does not need to "keep track" of the particular chain contour passing through each volume element. We can then use the translational symmetry in the x direction to restrict our attention to the region $(0, 2\pi/q)$. The elastic free energy F_e per unit area of lamellar reads

$$\frac{F_e}{k_B T} = \frac{K}{2}\frac{q}{2\pi}\int_0^{2\pi/q}\mathrm{d}x \int_{z_l}^{z_u}\mathrm{d}z\, \mathbf{E}^2 \tag{7}$$

with the constant $K = 3\upsilon^{-1} l_p^{-2}$ and l_p the persistence length of the polymer in units of b.

The equation satisfied by the chain tension $\mathbf{E}$ and the form of the free energy suggest an analogy between the stretching field and the electric field between two charged sheets. The conservation equations play the role of the Poisson equation and the density of chain sources ρ that of the charge density. As in electrostatics, the Poisson equation provides a relation between the normal component of the field at each surface of the lamella and the number of chain ends per unit area (the surface charge) σ.

$$\mathbf{E}_n = \upsilon\sigma \tag{8}$$

However, this electrostatic analogy is broken by the additional constraint that each polymer must use exactly N monomers in traveling from the lower to the upper surface. Each polymer contour C starts at the point $(x_i, z_l(x_i))$ and travels to the point $(x_f, z_u(x_f))$ and we can write this constraint as an integral along the polymer contour

$$\int_C \mathrm{d}l\, |\mathbf{E}|^{-1} = N \tag{9}$$

We can then change variables from l, describing the contour length, to the height z and write the condition of conservation of monomers for all polymers in the system as

$$\int_{z_l(x_i)}^{z_u(x_f)} \mathrm{d}z \frac{1}{E_z(x_c, z)} = N \tag{10}$$

where $x_c(z)$ is the x coordinate of the chain contour, which starts at x_i, as a function of z.

The equilibrium configuration of the chains is obtained by minimization of the elastic free energy with respect to $\mathbf{E}$ subject to the constraints (6) and (10). These constraints are most easily imposed by introducing two Lagrange multiplier fields $\phi(\mathbf{r})$ and $g(x)$.[7] Thus we minimize the following functional G, where we have set $x = x_i$:

$$\begin{aligned} G = \frac{K}{2}\int_0^{2\pi/q}\mathrm{d}x \int_{z_l(x)}^{z_u(x)}\mathrm{d}z\, \mathbf{E}^2 + \\ \int_0^{2\pi/q}\mathrm{d}x\, g(x)\left(\int_{z_l(x)}^{z_u(x_f)} \frac{1}{E_z(x_c, z)}\,\mathrm{d}z - N\right) - \\ K\int_0^{2\pi/q}\mathrm{d}x \int_{z_l(x)}^{z_u(x)} \mathrm{d}z\, \phi(\mathbf{r})(\nabla\cdot\mathbf{E}) \end{aligned} \tag{11}$$

To proceed with the standard Euler–Lagrange minimization we would need all the terms in (11) to involve integrals over the same region. We note that the second term on the right-hand side of (11) involves x_f and x_c, which are not necessarily interchangeable with $x = x_i$. However, we can proceed by assuming that $z_u(x_f) = z_u(x) + O(\epsilon_u^2)$ and $E_z(x_c, z) = E_z(x, z) + O(\epsilon_u^2)$, reassuring the reader that these relationships will later be derived rigorously. If we restrict ourselves to zeroth or first order in ϵ_u, we can thus ignore the difference between x_f, x_c, and $x = x_i$. In what follows we also assume that ϵ_l is of the same order of magnitude as ϵ_u.

The standard Euler–Lagrange minimization procedure[12] for the free energy functional G gives the following Euler equations, which we again emphasize are strictly true only for terms of zeroth or first order in ϵ_u.

$$E_x = -\frac{\partial}{\partial x}\phi \tag{12}$$

$$E_z = -\frac{\partial}{\partial z}\phi + K^{-1}E_z^{-2}g(x) \qquad (13)$$

Here the Lagrange multiplier $\phi(\mathbf{r})$ roughly plays the role of the electrostatic potential. However, due to the monomer conservation constraint for each chain (10), the relation between the field $\mathbf{E}$ and $\phi(\mathbf{r})$ is not the classical relation $\mathbf{E} = -\nabla\phi(\mathbf{r})$.

The equations for the chain tensions must be solved subject to the constraints (6) and (10) as well as the additional boundary condition that there can be no tangential stretching at either of the surfaces; the polymer ends are not grafted at the lamella surfaces and the chain ends are free to move along the surfaces. This final condition leads to the following equations at the lamella surfaces:

$$E_t(x,z_i) = 0 \qquad (14)$$

where E_t denotes the component of $\mathbf{E}$ tangential to the surface and $i = \mathrm{u,l}$ labels the two lamella surfaces. In the limit of small deformations, we can express E_t as a function of the x and z components

$$E_t(x,z_i) = E_x - \epsilon_i q \sin qx E_z + O(\epsilon_u^{\,2}) \qquad (15)$$

where we assume that $\epsilon_i q \ll 1$. This expansion is therefore only valid when the slope of the lamella surfaces remains small.

We now solve the Euler equations for the chain conformations pertubatively in ϵ_u. The expansions of the relevant physical quantities in powers of ϵ_u are written as

$$E_x(x,z) = E_x^{(0)} + \epsilon_u E_x^{(1)} + \epsilon_u^{\,2}E_x^{(2)} + \ldots \qquad (16a)$$

$$E_z(x,z) = E_z^{(0)} + \epsilon_u E_z^{(1)} + \epsilon_u^{\,2}E_z^{(2)} + \ldots \qquad (16b)$$

$$\phi(x,z) = \phi^{(0)} + \epsilon_u\phi^{(1)} + \epsilon_u^{\,2}\phi^{(2)} + \ldots \qquad (16c)$$

$$g(x) = g^{(0)} + \epsilon_u g^{(1)} + \epsilon_u^{\,2}g^{(2)} + \ldots \qquad (16d)$$

The number of chains per unit area can then be calculated from the chain tensions using eq 8; it is also expanded in powers of ϵ_u

$$\sigma(x) = \sigma^{(0)} + \epsilon_u\sigma^{(1)} + \epsilon_u^{\,2}\sigma^{(2)} + \ldots \qquad (16e)$$

2.1. Chain Conformation in a Deformed Lamella.

At zeroth order in ϵ_u, the lamella is flat and it is a simple process to show that the conformation of the chains is described by the following expressions which are solutions to eqs 6, 10, 12, 13, and 14. Similar results are already well-known for flat grafted polymer brushes.[7]

$$E_x^{(0)} = 0 \qquad (17a)$$

$$E_z^{(0)} = h/N \qquad (17b)$$

$$g^{(0)} = 0 \qquad (17c)$$

$$\phi^{(0)}(z) = -\left(\frac{h}{N}\right)z \qquad (17d)$$

$$\sigma^{(0)} = h/(Nv) \qquad (17e)$$

We then seek solutions to (12) and (13) at first order in ϵ_u. At this order (12) and (13) yield the following equations, respectively:

$$E_x^{(1)} = -\frac{\partial\phi^{(1)}}{\partial x} \qquad (18)$$

$$E_z^{(1)} = -\frac{\partial\phi^{(1)}}{\partial z} + K^{-1}(h/N)^{-2}g^{(1)}(x) \qquad (19)$$

These equations are solved in Appendix A.

2.2. Free Energy of Deformation.

We now calculate the total free energy of a deformed lamella. It is the sum of the elastic contribution and of the interfacial free energy associated with the change in area of the A–B interface.

The elastic free energy of the lamella is given by eq 7, which we now expand in powers of ϵ_u to second order.

$$F_e = F_e^{(0)} + \frac{\epsilon_u}{h}F_e^{(1)} + \left(\frac{\epsilon_u}{h}\right)^2 F_e^{(2)} + \ldots \qquad (20)$$

The zeroth-order contribution $F_e^{(0)}$ is the free energy of a flat lamella with the same average thickness h

$$\frac{F_e^{(0)}}{k_B T} = \frac{K}{2}\frac{q}{2\pi}\int_0^{2\pi/q}\mathrm{d}x\int_0^h \mathrm{d}z\, E_z^{(0)2} = \frac{K}{2}h(h/N)^2 \qquad (21)$$

The first-order contribution to the free energy vanishes when integrated over the period of the undulation. Finally, we write the contribution at second order in ϵ_u as a sum of two terms

$$F_e^{(2)} = F_{e1}^{(2)} + F_{e2}^{(2)} \qquad (22)$$

The first term $F_{e1}^{(2)}$ involves only the chain tensions at first order in ϵ_u and is defined as

$$\frac{F_{e1}^{(2)}}{k_B T} = \frac{K}{2}\frac{q}{2\pi}h^2\int_0^{2\pi/q}\mathrm{d}x\,[\int_0^h(E_x^{(1)2} + E_z^{(1)2})\,\mathrm{d}z + 2E_z^{(0)}\cos qx(E_z^{(1)}(x,h) - (\epsilon_l/\epsilon_u)E_z^{(1)}(x,0))] \qquad (23)$$

This can be readily calculated using the results of Appendix A.

$$\frac{F_{e1}^{(2)}}{F_e^{(0)}} = \left(2(1-\epsilon_l/\epsilon_u)^2 + \frac{qh}{\sinh qh}\left(\epsilon_l/\epsilon_u - \frac{1+(\epsilon_l/\epsilon_u)^2}{2}\cosh qh\right)\right) \qquad (24)$$

The second term $F_{e2}^{(2)}$ involves the z component of the chain tension at second order and is equal to

$$\frac{F_{e2}^{(2)}}{k_B T} = \frac{K}{2}\frac{q}{2\pi}h^2\int_0^{2\pi/q}\mathrm{d}x\int_0^h 2E_z^{(0)}E_z^{(2)}\,\mathrm{d}z \qquad (25)$$

Although we have not calculated the tension $\mathbf{E}$ to second order, we show in Appendix B that this contribution to the free energy vanishes exactly.

To determine the contribution to the total free energy due to the distortion of the A–B interface we must first determine the position of this interface. We write the z coordinate of the interface z_{AB} as

$$z_{AB}(x) = \frac{h}{2} + \delta\cos qx \qquad (26)$$

The deformation of the interface δ is then determined by imposing that the A–B junction of each polymer chain lies at $N/2$ monomers along the chain.

$$\int_{z_l(x)}^{z_{AB}(x)}\mathrm{d}z\,\frac{1}{E_z(x,z)} = \frac{N}{2} \qquad (27)$$

Here also at lowest order in ϵ_u we can ignore the difference between the actual coordinate x_c of a given chain contour at a height z and the position of the first monomer $x = x_i$. To leading order in ϵ_u we find

$$\delta = (\epsilon_u + \epsilon_l)\left(1 - \frac{1}{2\cosh\frac{qh}{2}}\right) + O(\epsilon_u^{\,2}) \qquad (28)$$

The area of the A–B interface at the location z_{AB} is larger than the area projected onto the x–y plane by a factor $1 + \delta^2 q^2/4$. The interfacial free energy per unit area associated with the A–B contacts is then

$$\frac{F_{\mathrm{AB}}}{k_{\mathrm{B}}T} = \gamma_{\mathrm{AB}}\left(1 + \frac{\delta^2 q^2}{4}\right) \tag{29}$$

where we have introduced the surface tension $k_{\mathrm{B}}T\gamma_{\mathrm{AB}}$ which acts at the A–B interface. The interfacial free energy F_{AB} is expanded in powers of ϵ_{u}/h as

$$F_{\mathrm{AB}} = F_{\mathrm{AB}}^{(0)} + \left(\frac{\epsilon_{\mathrm{u}}}{h}\right)^2 F_{\mathrm{AB}}^{(2)} + ... \tag{30}$$

where

$$\frac{F_{\mathrm{AB}}^{(0)}}{k_{\mathrm{B}}T} = \gamma_{\mathrm{AB}} \tag{31}$$

and

$$\frac{F_{\mathrm{AB}}^{(2)}}{F_{\mathrm{AB}}^{(0)}} = \frac{(qh)^2}{4}(1 + \epsilon_{\mathrm{l}}/\epsilon_{\mathrm{u}})^2\left(1 - \frac{1}{2\cosh\frac{qh}{2}}\right)^2 \tag{32}$$

The total free energy per unit area associated with the deformed lamella $F_{\mathrm{tot}} = F_{\mathrm{e}} + F_{\mathrm{AB}}$ is the sum of the two contributions F_{e} (given by (21) and (24)) and F_{AB} (given by (31) and (32)). In fact, it is the free energy *per unit volume* of polymeric material $F_{\mathrm{V}} + F_{\mathrm{tot}}/h$ that determines the equilibrium behavior of the lamella. However, in the next section we show that, to order $(\epsilon_{\mathrm{u}}/h)^2$, F_{V} is directly proportional to F_{tot}. Equivalently, h can be treated as a constant (the flat lamella thickness, h_{flat}) for the purposes of calculating the free energy per unit volume to this order.

2.3. Free Energy per Unit Volume.

We first determine the equilibrium thickness h_{flat} of a flat lamella by minimizing its free energy per unit volume. Using (21) and (31), the free energy per unit volume of a flat lamella F_{V} reads

$$F_{\mathrm{V}}(h_{\mathrm{flat}}) = \frac{1}{h_{\mathrm{flat}}}\left[\frac{K}{2}h_{\mathrm{flat}}(h_{\mathrm{flat}}/N)^2 + \gamma_{\mathrm{AB}}\right] \tag{33}$$

The equilibrium thickness is obtained by minimization

$$h_{\mathrm{flat}} = \left(\frac{N^2\gamma_{\mathrm{AB}}}{K}\right)^{1/3} \tag{34}$$

The free energy per unit area of a flat lamella F_{flat} can be calculated from (21), (31), and (34).

$$\frac{F_{\mathrm{flat}}}{k_{\mathrm{B}}T} = \frac{3\gamma_{\mathrm{AB}}}{2} \tag{35}$$

We now consider the free energy per unit volume F_{V} of a roughened lamella. The average thickness of the lamella is h and the free energy per unit volume is $F_{\mathrm{V}}(h) = F_{\mathrm{tot}}(h)/h$, where F_{tot} is the total free energy per unit area calculated above. The average thickness of the lamella h is close to the equilibrium thickness of the same lamella on a flat surface h_{flat}, and so we write $h = h_{\mathrm{flat}}(1 + \epsilon)$, where ϵ is a small parameter. We then substitute for h in the free energy per unit volume and expand in powers of ϵ. Using our expressions for $F_{\mathrm{e}}^{(0)}$ (eq 21), $F_{\mathrm{AB}}^{(0)}$ (eq 31), $F_{\mathrm{e}}^{(2)}$ (eq 24), and $F_{\mathrm{AB}}^{(2)}$ (eq 32), we find

$$F_{\mathrm{V}}(h) = F_{\mathrm{V}}(h_{\mathrm{flat}}) + O(\epsilon^2) \tag{36}$$

On symmetry grounds it can be argued[13] that ϵ can only contain even powers of $\epsilon_{\mathrm{u}}/h_{\mathrm{flat}}$; hence ϵ must be smaller than or of the order of $(\epsilon_{\mathrm{u}}/h_{\mathrm{flat}})^2$ and eq 36 leads directly to

$$F_{\mathrm{V}}(h) = F_{\mathrm{V}}(h_{\mathrm{flat}}) + O(\epsilon_{\mathrm{u}}/h_{\mathrm{flat}})^4 = \frac{F_{\mathrm{tot}}(h_{\mathrm{flat}})}{h_{\mathrm{flat}}} + O(\epsilon_{\mathrm{u}}/h_{\mathrm{flat}})^4$$

In the following, we will thus set $h = h_{\mathrm{flat}}$ throughout.

It is convenient to rescale the free energy by the free energy of a flat lamella and to define the reduced free energy $\mathcal{F}$ as

$$\mathcal{F}(\epsilon_{\mathrm{u}},\epsilon_{\mathrm{l}},q) = \frac{F_{\mathrm{tot}}(\epsilon_{\mathrm{u}},\epsilon_{\mathrm{l}},q) - F_{\mathrm{flat}}}{F_{\mathrm{flat}}} \tag{37}$$

At second order in ϵ_{u}/h we obtain

$$\mathcal{F} = \frac{u}{2}(\epsilon_{\mathrm{u}}^2 + \epsilon_{\mathrm{l}}^2) - w\epsilon_{\mathrm{u}}\epsilon_{\mathrm{l}} \tag{38}$$

with u and w defined as

$$u = \frac{1}{3h^2}\left[4 - \frac{qh\cosh qh}{\sinh qh} + (qh)^2\left(1 - \frac{1}{2\cosh\frac{qh}{2}}\right)^2\right] \tag{39}$$

$$w = \frac{1}{3h^2}\left[4 - \frac{qh}{\sinh qh} - (qh)^2\left(1 - \frac{1}{2\cosh\frac{qh}{2}}\right)^2\right] \tag{40}$$

The free energy $\mathcal{F}$ is symmetric both under the exchange $\epsilon_{\mathrm{u}} \rightleftarrows \epsilon_{\mathrm{l}}$ and under sign reversal of ϵ_{u} and ϵ_{l}.

In the limit of long-wavelength deformations ($qh \ll 1$) the free energy $\mathcal{F}$ may be expanded in powers of qh. We find the following asymptotic behavior:

$$\mathcal{F} = \left(\frac{1}{h}\right)^2\left(\frac{(\epsilon_{\mathrm{u}} - \epsilon_{\mathrm{l}})^2}{2} - \frac{(\epsilon_{\mathrm{u}} - \epsilon_{\mathrm{l}})^2}{72}(qh)^2 + \frac{61\epsilon_{\mathrm{u}}^2 + 118\epsilon_{\mathrm{u}}\epsilon_{\mathrm{l}} + 61\epsilon_{\mathrm{l}}^2}{4320}(qh)^4 + O(qh)^6\right) \tag{41}$$

If we consider the undulation mode of the lamella where the two surfaces are oscillating in phase and with the same amplitude ($\epsilon_{\mathrm{u}} = \epsilon_{\mathrm{l}}$), the dominant contribution to the free energy is proportional to $(qh)^4$. This corresponds to a bending free energy proportional to the square of the local curvature of the lamella $q^2\epsilon_{\mathrm{u}}$. This scaling is consistent with the behavior of smectic liquid crystals, where it is well-known[14] that there is no surface tension term proportional to $(qh)^2$ in the free energy. The bending modulus k_{c}, obtained from the free energy (41), is

$$\frac{k_{\mathrm{c}}}{k_{\mathrm{B}}T} = \frac{\gamma_{\mathrm{AB}}}{3}h^2 \sim N^{4/3} \tag{42}$$

It has the same scaling behavior as the bending modulus of grafted polymer layers obtained in refs 15.

In the limit of small-wavelength deformations

$$\mathcal{F} = \left(\frac{1}{h}\right)^2\left(\frac{1}{6}\right)[-qh(\epsilon_{\mathrm{l}}^2 + \epsilon_{\mathrm{u}}^2) + (qh)^2(\epsilon_{\mathrm{u}} + \epsilon_{\mathrm{l}})^2] \tag{43}$$

The free energy is dominated by the surface tension of the A–B interface. Notice that the first correction due to the elasticity of the chains is negative in our model.

2.4. A Single Lamella at a Rough Surface.

In this section we consider a single lamella with its lower surface in contact with a sinusoidally rough surface. Thus the undulation of the lower surface ϵ_{l} is imposed. We want to find the equilibrium undulation of the upper surface ϵ_{u} as a function of the dimensionless wavevector qh.

We first introduce a dimensionless parameter $\alpha = \epsilon_{\mathrm{u}}/e_{\mathrm{l}}$. The experimental quantity measured by grazing incidence X-ray scattering is the ratio of the intensities scattered by the upper surface and the lower surface and is equal to α^2. To determine the equilibrium value α_{min} (and therefore

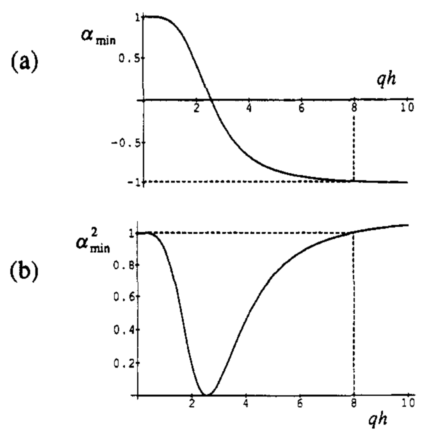

Figure 1. (a) Variation of the roughness ratio $\alpha_{\min}$ as a function of the dimensionless wavevector qh; the dotted line shows the point at which $\alpha_{\min} = -1$. (b) Variation of the experimental ratio $\alpha_{\min}{}^2$ as a function of qh; the dotted line shows the point at which $\alpha_{\min}{}^2 = 1$.

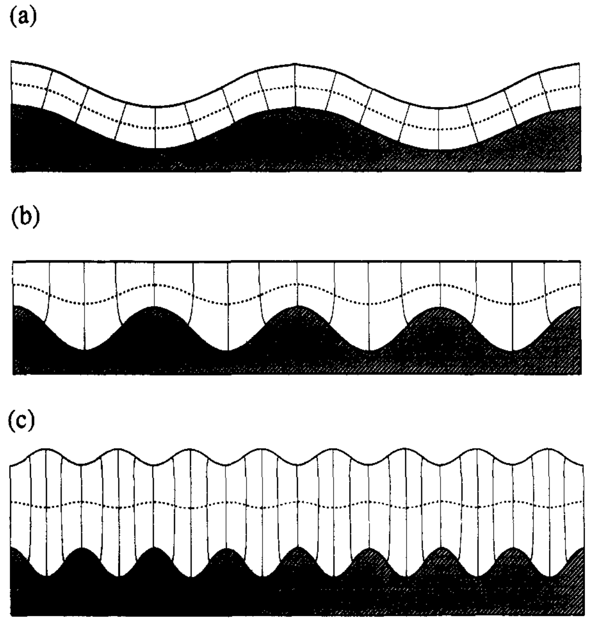

Figure 2. Conformation of a lamella layer assembled on a sinusoidal surface at various values of the wavevector q: (a) long-wavelength undulations, $q < q_c$; (b) undulations at the special wavelength $q = q_c$; (c) undulations at short wavelengths $q > q_c$. The polymer contours are shown (note that they leave the lamellar surfaces in a normal direction), as is the A–B interface, shown as a dotted line.

ϵ_u) we minimize the free energy (38) with respect to α.

$$\alpha_{\min}(qh) = w/u \tag{44}$$

The variations of both $\alpha_{\min}$ and the experimental intensity ratio $\alpha_{\min}{}^2$ with the dimensionless wavevector qh are shown in Figure 1. We now discuss the main features appearing on this plot.

(i) As $qh \rightarrow 0$, $\alpha_{\min} = 1 - (qh)^4/18$. For large wavelength deformations, the upper surface of the lamella follows closely the undulations of the lower surface (see Figure 2a). This remains true provided the wavelength of the undulation is smaller than a certain healing length which is of the order of the lamellar thickness h. This behavior may be compared to the behavior of thin liquid films on a rough solid surface as studied in ref 16. The roughness of a thin liquid film also follows the roughness of the solid surface if the wavelength is larger than a healing length that describes the competition between the interfacial tension at the surface of the film and the direct long-range interactions between solid and liquid. Two differences should be noted however: for a liquid film the ratio of the roughnesses $\alpha_{\min}$ has a Lorentzian decay with the wavevector; the smoothening of the upper interface is due to surface tension as well but the surface tension acts at the upper surface of the film and not at the midplane as in the case of a copolymer lamella.

(ii) Contrary to what happens for thin liquid films, where one finds that the ratio $\alpha_{\min}$ decreases monotonically to zero as the wavevector increases, for a single lamella $\alpha_{\min}$ vanishes at a finite wavevector q_c such that $q_c h \approx 2.6$ (see Figure 2b). For $q > q_c$ we observe that $\alpha_{\min}$ becomes negative and the upper surface undulates out of phase of the lower surface (see Figure 2c). In the limit where qh becomes very large, $\alpha_{\min} = -1$ and $\epsilon_u = -\epsilon_l$. As mentioned following (43), the interfacial contribution to the free energy of the lamella scales more strongly with qh in the large q (small wavelength) limit. The surface where the interfacial tension acts, i.e., the midplane of the lamella, must therefore become flat as $qh \rightarrow \infty$. This requires the two surfaces of the lamella to be symmetric with respect to the A–B interface; i.e., $\alpha_{\min} = -1$. Since the roughness ratio $\alpha_{\min}$ is equal to 1 when $qh = 0$ and to -1 when qh is large, there exists a critical value of the wavevector q_c at which it vanishes. For this precise value of the wavevector, the upper surface of the lamella is flat, $\epsilon_u = 0$ (see Figure 2b).

(iii) For $qh > q^*h \approx 8.0$ we find $\alpha_{\min} < -1$. When the wavevector is large, $\alpha_{\min}$ approaches -1 from below; the amplitude of the undulation of the upper surface is larger than the imposed amplitude of the undulation of the lower surface. This quite unexpected result is due to the negative sign of the elastic correction to the interfacial energy in the lamella free energy (43). However, as discussed in section 5, we believe that this is an artifact of the Alexander–de Gennes approximation and that a more rigorous theory would predict a value of $\alpha_{\min}$ that approaches -1 from above.

3. A Lamella Stack at a Rough Surface

In this section we study the behavior of a lamellar stack where the lowest lamellar surface is in contact with a sinusoidally rough substrate. We seek to determine both the free energy associated with the stack and the penetration depth ξ of the roughness of the interface between lamellae induced by the substrate. It has been shown that when two polymer brushes are in contact, the chains of the two layers do not significantly interpenetrate.[17] We can thus treat the chain conformations in each layer independently and consider that for each layer the undulation of the upper surface ϵ_u is identical to the undulation of the lower surface ϵ_l of the lamella directly above. We define the z coordinate of the interface between the ith and the (i+1)th lamella layer to be z_i.

$$z_i(x) = ih + \epsilon_i \cos qx \tag{45}$$

The total free energy of an infinite stack is the sum of the free energies of the individual lamellae. Taking as a reference state the free energy of flat lamellae, we will consider here the reduced free energy

$$\mathcal{F}_{\text{stack}} = \sum_{i=1}^{\infty} \mathcal{F}_i \tag{46}$$

where $\mathcal{F}_i$ is the value of $\mathcal{F}$ for the ith layer given by eq 38 where we replace ϵ_l by ϵ_{i-1} and ϵ_u by ϵ_i.

It is interesting to notice that in the limit of small wavevectors this free energy has the same structure as the standard elastic free energy of smectic A liquid crystals.

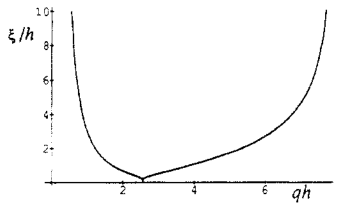

Figure 3. Penetration depth of the roughness induced by the surface ξ (in units of the lamella thickness h) into an infinite lamella stack as a function of the dimensionless wavevector qh.

If we introduce the continuous variable z (replacing the layer index i) and define $\epsilon(z)$ as the continuous extension of the deformation of the interface between lamellae at a height z, eqs 46 and 41 are equivalent to the following free energy density for ($qh \ll 1$):

$$\frac{f}{k_BT} = \frac{1}{2}B\left(\frac{\partial\epsilon}{\partial z}\right)^2 + \frac{1}{2}K_1\left(\frac{\partial^2\epsilon}{\partial x^2}\right)^2 + A\left(\frac{\partial^2\epsilon}{\partial x\partial z}\right)^2 \quad (47)$$

The compressional modulus of the smectic is $B = 3\gamma_{AB}/h$ and the splay constant is $K_1 = k_c/h = \gamma_{AB}h/3$, where k_c is the bending modulus of one layer given by (42). The last term is a higher order coupling between bending and compression.

The equilibrium deformation of the layers is obtained by minimization of the stack free energy with respect to ϵ_i.

$$\partial\mathcal{F}_{\text{stack}}/\partial\epsilon_i = 2u\epsilon_i - w(\epsilon_{i+1} + \epsilon_{i-1}) = 0 \quad (48)$$

The general form of the deformation of the ith lamella is

$$\epsilon_i = \epsilon_0\tilde{\alpha}^i$$

where ϵ_0 is the imposed roughness of the lowest lamella and

$$\tilde{\alpha} = \frac{u}{w} \pm \left[\left(\frac{u}{w}\right)^2 - 1\right]^{1/2} = {\alpha_{\min}}^{-1} \pm [{\alpha_{\min}}^{-2} - 1]^{1/2} \quad (49)$$

where $\alpha_{\min}$ has been defined in eq 44.

The choice of the sign in (49) is made by imposing that the modulus of $\tilde{\alpha}$ is smaller than one. The actual value of $\tilde{\alpha}$ depends on the wavevector q of the imposed undulation. If $q < q_c$, where q_c is the wavevector defined in section 2.4 for which $\alpha_{\min} = 0$, we have

$$\tilde{\alpha}(qh) = \frac{u}{w} - \left[\left(\frac{u}{w}\right)^2 - 1\right]^{1/2} \quad (50)$$

whereas if $q_c < q < q^*$, where q^* is the wavevector for which $\alpha_{\min} = -1$, we find instead

$$\tilde{\alpha}(qh) = \frac{u}{w} + \left[\left(\frac{u}{w}\right)^2 - 1\right]^{1/2} \quad (51)$$

Finally, for $q > q^*$ there does not exist any solution with a deformation decaying in amplitude.

The smectic penetration depth ξ is the distance that the roughness propagates into the lamella stack. Thus ξ is given by

$$\xi = h\frac{-1}{\log|\tilde{\alpha}|} \quad (52)$$

A plot of the penetration depth as a function of the wavevector is given in Figure 3. In the limit of small wavevectors ($qh \ll 1$) the penetration depth diverges as q^{-2} and we recover the classical result for smectic liquid crystals $\xi = 3/(q^2h)$. At $q = q_c$ the upper surface of the first lamella is flat and therefore all the other lamellae are flat and ξ vanishes. As q increases further, the midplane of the lamellae becomes flatter and flatter and the two surfaces of the same lamella undulate out of phase; the penetration depth increases and diverges when $q = q^*$. When $q > q^*$ the model predicts that the lamellar phase is unstable. This again is related to the negative value of the elastic contribution to the free energy in eq 43; we believe that this is an artifact of the model.

It should also be noticed that the experimentally observable interfaces are not the surfaces between lamellae but the A–B interfaces of the lamellae. According to (28) the undulation of the midplanes is

$$\delta = \epsilon_0\tilde{\alpha}^{i-1}(1 + \tilde{\alpha})\left(1 - \frac{1}{2\cosh\frac{qh}{2}}\right) \quad (53)$$

The penetration depth of these undulations is identical to that for the penetration of the undulations at the lamellar interfaces ($\xi = 3/(q^2h)$ in the small-q limit).

The stack free energy is calculated from eq 46; we find

$$\mathcal{F}_{\text{stack}} = {\epsilon_0}^2\frac{(u/2)(1 + \tilde{\alpha}^2) - w\tilde{\alpha}}{1 - \tilde{\alpha}^2} \quad (54)$$

which has the following asymptotic behavior for $qh \ll 1$:

$$\mathcal{F}_{\text{stack}} = \left(\frac{\epsilon_0}{h}\right)^2\left(\frac{(qh)^2}{6} + O(qh)^4\right) \quad (55)$$

The free energy of a single lamella is dominated by the bending term proportional to q^4; when integrated over a penetration depth $\xi \sim q^{-2}$, this gives a total free energy proportional to q^2.

4. Effect of Polymer/Air and Polymer/Surface Interactions

In section 2.4, we have calculated the equilibrium lamella thickness, without defining precisely the geometry of the system, i.e., whether the polymer assembles to form a single lamella next to a surface, in which case h governs the total area (at fixed volume V), or the polymer assembles to form a lamellar stack, in which case the area of each layer is fixed but the total number of layers depends on their thickness. However, if one wishes to consider a more complex system, e.g., one in which the uppermost lamella surface is in contact with air, it *is* necessary to define the geometry of the system. For a thick enough stack, an air interface at the top of the stack has no effect; since the top layer is flat and has constant area, it merely amounts to a (constant) offset to the total free energy. However, the stack may be chosen[18] so as to have sufficiently few layers that the upper layer is still rough; i.e., the stack height H and the penetration depth of the roughening ξ obey the inequality $H \lesssim \xi$. In this case the air interface, with an associated surface tension γ_{air}, has the effect of smoothing out the roughness. For the case of a single lamella assembled on an infinite surface, the air interfacial tension modifies the equilibrium behavior at *zeroth order* in ϵ_u/h: we must replace γ_{AB} by $\gamma_{AB} + \gamma_{\text{air}}$. The air interfacial tension also contributes to the smoothening of the roughness at the upper interface (i.e., it reduces ϵ_u).

Note also that we have neglected any interaction between the surface and the polymer making up the lamella. In general, another surface tension γ_{surface} exists at the polymer/substrate interface. However, provided that the polymer always remains in contact with the surface, this has no effect for the case of a lamellar stack (as before it amounts to a constant offset to the free energy), and, for the case of the single layer, it has a similar effect to an air interface in modifying the overall surface tension acting on the layer.

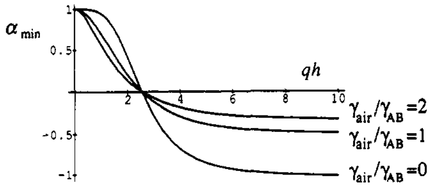

Figure 4. Variation of the roughness ration $\alpha_{\min}$ as a function of the dimensionless wavevector qh for various values of the ratio γ_{air}/γ_{AB}, as shown.

We now write down a free energy functional governing the behavior of small lamellar stacks, when the stack height H is less than or of the order of the penetration depth ξ. In this case we introduce a surface tension γ_{air} (in units of k_BT) which acts at the upper lamella surface. We expect this to damp the fluctuations at the uppermost surface. To determine the equilibrium properties of such a stack one must minimize the following functional:

$$\mathcal{F}_{\text{stack}} = \frac{2\gamma_{\text{air}}}{3\gamma_{\text{AB}}}(1 + \epsilon_n^{\,2}q^2/4) + \sum_{i=1}^{n}\mathcal{F}_i \tag{56}$$

where $\mathcal{F}_i$ is defined in (46).

While this functional can easily be minimized analytically for one layer, as the number of layers is increased the algebra quickly becomes very tedious and in practice one would resort to numerical methods. We will only proceed here to consider a single layer which shares many features with the behavior of small lamellar stacks.

For a single lamella layer we minimize the following rescaled free energy functional with respect to variation of ϵ_u:

$$\mathcal{G} = \frac{u}{2}(\epsilon_u^{\,2} + \epsilon_l^{\,2}) - w\epsilon_u\epsilon_l + \frac{\gamma_{\text{air}}}{6\gamma_{\text{AB}}}(\epsilon_u q)^2 \tag{57}$$

where u and w have been defined in (39) and (40). We obtain

$$\frac{\epsilon_u}{\epsilon_l} = \alpha_{\min} = \frac{w}{u + \dfrac{\gamma_{\text{air}}}{3\gamma_{\text{AB}}}q^2} \tag{58}$$

Figure 4 shows a plot of $\alpha_{\min}$ as a function of the dimensionless wavevector qh at various values of the ratio γ_{air}/γ_{AB}. When the wavevector is increased, $\alpha_{\min}$ decreases and vanishes at the critical wavevector q_c; it becomes negative at higher wavevectors, signifying that the two surfaces are undulating out of phase. In the limit of small wavevectors, the roughness ratio $\alpha_{\min}$ has the same structure as for simple liquid films on rough surfaces, $\alpha_{\min} = 1 - q^2\lambda^2$ with a healing length $\lambda = (\gamma_{air}/\gamma_{AB})^{1/2}h$. In the limit of large wavevectors, $\alpha_{\min}$ reaches a constant negative value, $\alpha_{\min} = -1/[1 + (\gamma_{air}/\gamma_{AB})]$. In the limit where γ_{air} vanishes, we recover the result (44) (see, for comparison, Figure 1a).

5. Discussion

We have discussed the properties of a diblock copolymer film in a lamellar phase on a rough substrate. When the film is made of a single lamella, the relevant physical property is the roughness ratio $\alpha_{\min}$. (The experimental quantity is $\alpha_{\min}^2$.) If the wavelength of the roughness is smaller than the lamellar thickness, the undulation of the upper surface follows the wavelength of the substrate and $\alpha_{\min}$ decreases with the wavevector. One of our main results is that the roughness ratio changes sign at the critical wavevector q_c. If the wavevector of the undulation is exactly q_c, the upper surface of the lamella is flat and the deformation is completely damped. If the wavelength of the undulation is small, $\alpha_{\min}$ is negative and the upper surface of the lamella shows an undulation out of phase with the imposed undulation on the surface. In the limit of infinite wavevectors $\alpha_{\min}$ reaches a negative constant value which is equal to -1 in the absence of an interfacial tension with air and larger than -1 in the presence of an interfacial tension with air which smooths the deformation of the upper surface.

Qualitatively similar results have been obtained for stacks of lamellae. At small wavevectors ($qh < 1$) the lamellar phase behaves as a classical smectic liquid crystal for which we have calculated the splay constant and the compressional modulus. As in usual smectics, the penetration depth of the undulation diverges when the wavevector vanishes as q^{-2}. At the wavevector q_c the first layer is flat and the deformation does not penetrate into the bulk of the lamellar phase; the penetration depth vanishes. At higher wavevectors consecutive layers have deformations of opposite signs and the penetration depth increases with the wavevector.

Another important result is that when the wavevector is larger than a second critical value q^*, the roughness ratio is smaller than -1; the undulation is not damped but amplified. This suggests that the lamellar phase is unstable with respect to undulations with a wavelength much smaller than the interlamellar spacing. One of the limitations of our work is that we have considered only small deformations of the lamellae and that we have calculated the free energies only at second order in the deformations. This instability of the lamellar phase might well be stabilized by higher order terms.

Another important limitation of our work is that we have used the Alexander–de Gennes theory of polymer brushes to describe the properties of the lamellae. In this model all the end monomers of the chains are located on the surfaces of the lamellae. A more refined theory of polymer brushes that treats self-consistently the end points of the chains has been proposed[10] and it has been shown that the Alexander–de Gennes theory does not give the absolute minimum of the free energy of polymer brushes. We now argue that the instability of the lamellar structure predicted at large wavevectors could be due to the fact that the Alexander–de Gennes picture only gives a local minimum of the free energy and is thus an artifact of our model.

The instability of the lamellar phase (values of the roughness ratio $\alpha_{\min} < -1$) is due to the negative sign of the elastic contribution to the free energy (43). If we look more carefully at the various terms in the elastic free energy given by eq 23, it can be seen that only one of these terms is negative and dominates all the others; this term is given by

$$\frac{F_{\text{surface}}}{k_BT} = \frac{K}{2}\frac{q}{2\pi}h^2\int_0^{2\pi/q}\mathrm{d}x\; 2E_z^{(0)}\cos qx(E_z^{(1)}(x,h) - (\epsilon_l/\epsilon_u)E_z^{(1)}(x,0))$$

It represents the contribution to the elastic energy at order $(\epsilon_u/h)^2$ from the material near each surface. It is the contribution, at this order, from the monomers in the "crests" minus that from the monomers in the "troughs" (at both surfaces). This term therefore depends critically on the chain tension **E** *at* the lamella surfaces. In the Alexander–de Gennes model, the chain tension does not vanish at the surface. In the more refined self-consistent treatment, the chains have a vanishing tension at their end points, which are free. All the monomers in the crests or the troughs of the undulations are close to the end points and their tension is certainly very small. It is thus reasonable to speculate that the negative term is strongly overestimated and that the actual value of the elastic energy is positive and remains proportional to qh. With this assumption the roughness ratio $\alpha_{\min}$ is larger than -1 and tends to -1 in the limit of infinite wavevector. Similarly, the lamellar phase is stable and the penetration depth increases with the wavevector and diverges for large wavevectors.

Another implicit approximation of both the Alexander–de Gennes model and the self-consistent field theory of polymer brushes is the strong tension approximation. Although this approximation is valid on average, it is not valid locally at the scale of the blobs. We thus do not expect the brush theories to give a good description of the chain elasticity at large wavevectors (when the wavelength is smaller than the blob size).

Finally, we note that nonlinear effects (such as induced harmonics) may be more important in real systems, in which the chain ends do not all terminate at the lamellar surface. In these systems the amplitude of the out-of-phase deformation for $q > q_c$ may diminish somewhat with increasing N.

Despite these limitations, we believe that our model describes at least qualitatively the behavior of copolymer films on rough substrates and that an experimental comparison is possible, perhaps using photoetching to construct a fairly crude roughened substrate. It also provides a framework for the study of dislocations in lamellar phases that certainly play a dominant role in the rheology of these phases.[19] By extending the present work to general lamella perturbations (a Fourier sum of q modes), it may be possible to calculate approximately the energy of an edge dislocations in the lamellar phase.[20]

Appendix A

In this appendix we solve the equations giving the chain tensions at first order in ϵ_u. Using (18) and (19), eq 6 translates, at first order in ϵ_u, to (59) below.

$$\nabla^2\phi^{(1)} = 0 \tag{59}$$

The condition (10) implies the following relation at first order in ϵ_u:

$$(h/N)(1 - \epsilon_l/\epsilon_u)\cos qx = \int_0^h E_z^{(1)}\,dz \tag{60}$$

Finally, we use the expansions (15) to write the boundary conditions (14) at first order.

$$E_x^{(1)}(x,0) = (\epsilon_l/\epsilon_u)(h/N)q\sin qx \tag{61a}$$

$$E_x^{(1)}(x,h) = (h/N)q\sin qx \tag{61b}$$

Equations 18, 19, 60, and 61 can be solved by separation of variables. The solutions, which can be checked by substitution, are found to be

$$E_x^{(1)}(x,z) = (h/N)q\sin qx\left(\frac{1 - (\epsilon_l/\epsilon_u)\cosh qh}{\sinh qh}\sinh qz + (\epsilon_l/\epsilon_u)\cosh qz\right) \tag{62}$$

$$E_z^{(1)}(x,z) = (h/N)q\cos qx\left(\frac{2(1 - \epsilon_l/\epsilon_u)}{qh} - \left(\frac{1 - (\epsilon_l/\epsilon_u)\cosh qh}{\sinh qh}\cosh qz + (\epsilon_l/\epsilon_u)\sinh qz\right)\right) \tag{63}$$

$$g^{(1)}(x) = \frac{2K}{h}(h/N)^3(1 - \epsilon_l/\epsilon_u)\cos qx \tag{64}$$

$$\phi^{(1)}(x,z) = (h/N)\cos qx\left(\frac{1 - (\epsilon_l/\epsilon_u)\cosh qh}{\sinh qh}\sinh qz + (\epsilon_l/\epsilon_u)\cosh qz\right) \tag{65}$$

The density of chain ends at each of the upper and lower surfaces (denoted σ_u and σ_l, respectively) can then be calculated from eq 8

$$\sigma_u^{(1)}(x) = (h/vN)q\cos qx\left(\frac{2(1 - \epsilon_l/\epsilon_u)}{qh} + \frac{\epsilon_l/\epsilon_u - \cosh qh}{\sinh qh}\right) \tag{66}$$

$$\sigma_l^{(1)}(x) = (h/vN)q\cos qx\left(\frac{2(1 - \epsilon_l/\epsilon_u)}{qh} - \frac{1 - (\epsilon_l/\epsilon_u)\cosh qh}{\sinh qh}\right) \tag{67}$$

Appendix B

In this appendix we show that the contribution $F_{e2}^{(2)}$ to the elastic free energy exactly vanishes. To calculate $F_{e2}^{(2)}$ directly one would have to calculate $E_z^{(2)}$ using the second-order terms for eqs 6, 10, 12, 13, and 14. Luckily this formidable task can be avoided by considering merely the second-order terms in the condition (10), as we now demonstrate.

As was mentioned in the discussion following eq 11, x_f, the chain's final x coordinate, and $x_c(z)$, the function describing the chain's x coordinates, are not necessarily interchangeable with x_i, the chain's initial x coordinate. Since we now wish to consider terms to second order in ϵ_u, we must consider more carefully the actual chain contour $x_c(z)$. Note that the results we derive here verify, a posteriori, the assumptions $z_u(x_f) = z_u(x_i) + O(\epsilon_u^2)$ and $E_z(x_c,z) = E_z(x_i,z) + O(\epsilon_u^2)$ made in the discussion following eq 11.

The coordinate x_c of the chain contour at a height z is defined by

$$\frac{\partial x_c}{\partial z} = \frac{E_x}{E_z} \tag{68}$$

For our purposes we need to expand x_c to first order in ϵ_u. Integrating (68) by separation of variables and relabeling $x = x_i$, we find

$$x_c(z) - x = \epsilon_u\int_0^z \frac{E_x^{(1)}(x,z')}{E_z^{(0)}}\,dz' + O(\epsilon_u^2) \tag{69}$$

The variable x_f appears in condition (10) only through $\cos qx_f$. We can use (69) to find $\cos qx_f$ by expanding around $x = x_i$.

$$\cos qx_f = \cos qx - \epsilon_u q\sin qx\int_0^h \frac{E_x^{(1)}(x,z')}{E_z^{(0)}}\,dz' \tag{70}$$

The variable x_c appears in the function $E_z(x_c,z)$ in condition (10) and so we need also to consider the expansion of $E_z(x_c,z)$, this time to second order in ϵ_u.

$$E_z(x_c,z) = E_z^{(0)} + \epsilon_u E_z^{(1)}(x,z) + \epsilon_u^2\left[E_z^{(2)}(x,z) + \frac{\partial E_z^{(1)}}{\partial x}\int_0^z \frac{E_x^{(1)}(x,z')}{E_z^{(0)}}\,dz'\right] \tag{71}$$

where we have again relabeled $x = x_i$.

We now pick out the terms in an expansion of (10) which appear at second order in ϵ_u. Hence, using the results (69), (70), and (71) above, (10) leads, with some algebra, to the following:

$$\int_0^h E_z^{(0)} E_z^{(2)}(x,z)\,\mathrm{d}z = \int_0^h \left(E_z^{(1)}(x,z)^2 - E_z^{(0)} \frac{\partial E_z^{(1)}}{\partial x} \int_0^z \frac{E_x^{(1)}(x,z')}{E_z^{(0)}}\,\mathrm{d}z' \right) \mathrm{d}z - E_z^{(0)} [E_z^{(1)}(x,h) - (\epsilon_l/\epsilon_u) E_z^{(1)}(x,0)] \cos qx - E_z^{(0)^2} q \sin qx \int_0^h \frac{E_x^{(1)}(x,z')}{E_z^{(0)}}\,\mathrm{d}z' \qquad (72)$$

We notice immediately that all the terms on the right-hand side of eq 72 can already be calculated directly. It only remains to substitute (72) into eq 25, and, with some algebra, we find that $F_{e2}^{(2)}$ vanishes exactly.

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