Shear of Diblock Copolymer Lamellae: Width Changes and Undulational Instabilities

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ABSTRACT: We investigate the effect of oscillatory shear on the lamellar spacing in melts of symmetric diblock copolymers in the strong segregation limit. We find that the equilibrium lamellar spacing decreases. The modulus due to entanglements plays an important role. We further argue that before equilibrium is reached the layers will show an undulational instability in the direction perpendicular to the velocity and the velocity gradient.

I. Introduction

Diblock copolymers are materials that consist of two different polymer chains irreversibly tethered together at one end. At high temperatures the two blocks are uniformly mixed. At low temperatures the chains are driven to phase separate for enthalpic reasons. Irreversible tethering makes macrophase separation impossible, and microphase separation into structures of the order of 100 Å is the result. The mesophases formed can be lamellae, ordered arrays of cylinders or spheres, and various bicontinuous phases.[1-4] They are analogous to phases formed in surfactant systems and also to phases formed by metallic alloys. However, the resulting structures are on a much larger spatial scale. In this study, we consider the effects of shear on melts of symmetric diblocks. Both blocks are assumed to have the same statistical segment length a, the same volume per monomer $v = a^3$, and the same number of monomers $N/2$. Shear is often used both to align the lamellae formed from such diblocks and to remove defects.[5,6] This produces approximately monocrystalline samples. Much of the theoretical work has been aimed at a different issue, i.e., the effect of shear on the order–disorder transition from the homogeneous phase to the weakly ordered lamellar phase.[7-14] Our interest here is in the strong segregation limit, in which the AB diblocks form distinct AB and BA lamellae separated by sharp interfaces. Each A or B section then forms a strongly stretched polymer brush.

We first study how oscillatory shear affects the lamellar spacing. When there is no shear, this spacing is determined by the competition between the AB interfacial energy, which favors few layers (and hence large spacing), and the chain stretching energy, which favors small spacings.[2] A simple-minded argument for the effect of shear is as follows. As illustrated in Figure 1, shear tilts each chain and stretches it more than in an unsheared lamella. To avoid this penalty, the lamellar spacing should decrease. This, in fact, is the correct answer, and in the following section we study this effect more quantitatively. Furthermore, we find that before equilibrium is reached, a long-lived undulational instability can occur. As illustrated in Figure 2, the layers undulate in an attempt to achieve their equilibrium spacing, in a way similar to that of smectics under tension.[15,16] In section III we study this shear-induced undulational instability.

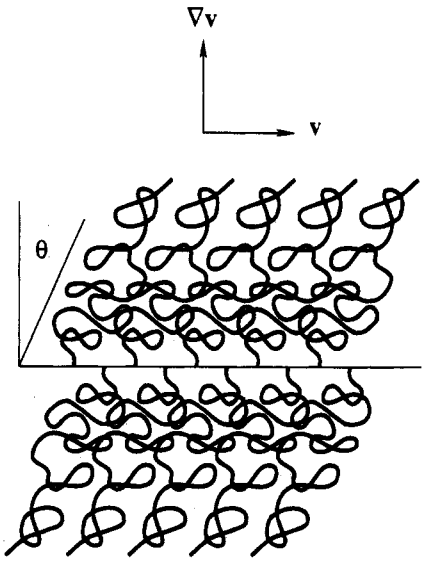

Figure 1. A single lamella under shear. The chains tilt through an angle θ in the plane of the velocity **v** and the velocity gradient ∇**v**.

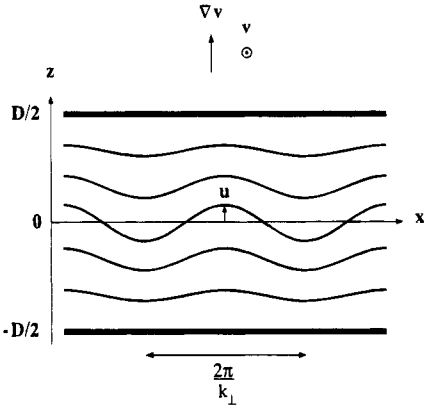

Figure 2. The shear-induced undulational instability. The shear velocity is perpendicular to the page. The undulations appear perpendicular to the velocity and the velocity gradient and have zero amplitude at the walls.

II. Lamellar Thickness Changes

We consider two plates separated by a distance D. The lower plate is stationary while the upper plate executes a displacement along its length with velocity $v(t) = V\cos(\omega t)$. We fix the shear stress exerted on the plate and allow the lamellar spacing to equilibrate. We examine the case of bulk samples. Thus, the number of layers n between the plates is very large. The lamellae interact via surface stresses. If we let the

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tangential force per unit area acting on the jth lamella due to the ith lamella be σ_{ij}, then by Newton's third law $\sigma_{ij} = -\sigma_{ji}$, where $j = i + 1$. We number the lamellae from the top down and let the top and bottom plates be designated by 0 and $n + 1$ respectively. The interaction between a lamella and a plate is different from that between two lamellae. We can formally avoid this difference by assuming the plates are half lamellae. This will not significantly change the physics and rids us of the need to study special boundary−layer effects.

We make a number of assumptions in the calculation. We assume that the system remains lamellar upon shear, i.e., that it does not radically change morphology into a different phase, as can happen, for instance, to lyotropic lamellar systems at high shear rates.[17] We also assume that the effect of an oscillatory shear is the same as the effect of a static shear, but with a different amplitude. This will be a reasonable approximation provided that the period of the oscillation is much less than the time required for chain exchange between layers. The most fundamental assumption is that the system is describable by a free energy. In this respect, we follow an approach similar to that of ref 18. Since the system is not in equilibrium it is unclear how good this approximation is. To go beyond this approximation it will be necessary to solve the time-dependent equations of motion.

First we write down the free energy of a single lamella of thickness L subject to a constant, applied shear stress σ at its top surface. An equal and opposite shear stress is applied at the base of the lamella. At high enough frequency the lamella behaves as a rubber-like solid with modulus μ and the chains tilt through an angle θ with respect to the surface normal. Thus, the Gibbs free energy per unit volume consists of four terms:

$$G = F_{\text{stretch}} + F_{\text{surface}} + F_{\text{deformation}} - \sigma \tan \theta \quad (1)$$

F_{stretch} is the stretching free energy of the chains. In the Alexander−de Gennes model,[19] this is

$$F_{\text{stretch}} = ({}^3/_2)kT/a^2(H^2/N)(Na^3)^{-1} \quad (2)$$

where $H = L/\cos\theta$ is the end-to-end distance of the chains, and the factor Na^3 is the volume of each chain. More sophisticated theories lead to numerical prefactor somewhat different from ${}^3/_2$.[2-4] This will not significantly change our results. The surface free energy per unit volume arises solely from the AB interface, and is given by $F_{\text{surface}} = \gamma/L$, where γ is the surface tension of that interface. These two terms are the only ones present in an unsheared lamella. The deformation term arises from entanglements within the lamellae. It has the form $F_{\text{deformation}} = {}^1/_2\mu \tan^2 \theta$. The final term is due to the work performed by the applied shear stress.

For the unsheared lamellae, minimization of G over L gives

$$L_0^3 = \gamma N^2 a^5/(3kT) \quad (3)$$

It is convenient to express the free energy per unit volume in terms of L_0, so that

$$G = \gamma/2(L^2/L_0^3)(1 + \tan^2 \theta) + \gamma/L + {}^1/_2\mu \tan^2 \theta - \sigma \tan \theta \quad (4)$$

The equilibrium angle of tilt is determined by minimizing this free energy. Thus,

$$\tan \theta_m = \sigma/(\mu + \gamma L^2/L_0^3) \quad (5)$$

at which the free energy is given by

$$G = \gamma/2(L^2/L_0^3) + \gamma/L - \sigma^2/[2(\gamma L^2/L_0^3 + \mu)] \quad (6)$$

This can be written in dimensionless form:

$$G = (\gamma/L_0)\,[{}^1/_2x^2 + x^{-1} - {}^1/_2S^2/(x^2 + U)] \quad (7)$$

where $x \equiv L/L_0$, $S \equiv \sigma L_0/\gamma$, and $U \equiv \mu L_0/\gamma$ are dimensionless measures of the lamellar spacing, shear stress, and shear modulus, respectively. In general, U will be much greater than unity. This is because $\mu \approx kTc_{\text{entanglement}}$, where

$$c_{\text{entanglement}} = (N/N_e)(1/Na^3) \quad (8)$$

is the number of entanglements per unit volume. Here N_e is the distance, in monomers, between each entanglement on a chain, and $(Na^3)^{-1}$ is the number of chains per unit volume. For a surface tension γ of order kT/a^2, and the value of L_0 given above, we find that $U \approx N^{2/3}/N_e$. Estimates of N_e range from 10 to 100. Thus, unless the chain is very short, $U \gg 1$.

We assume that inertial effects are unimportant, so that, by Newton's second law, $\sigma_{i-1,i} + \sigma_{i+1,i} = 0$. By Newton's third law, we find all the shear stresses must be equal:

$$\sigma_{i,i+1} = \sigma_{i+1,i+2} = \sigma_{i+2,i+3} \quad (9)$$

The case of fixed external shear stress can now be examined. In this case, the stress S across each layer is fixed, and from the free energy in eq 7, it is clear that the shear causes a decrease in the lamellar spacing. Assuming the change is small, we write $x = 1 + \epsilon$. The change in spacing is determined by optimization of eq 7:

$$\epsilon_{\text{min}} = -S^2(1 + U)/(3 + 9U + 9U^2 + 3U^3 - 3S^2 + S^2U) \approx -S^2/[(S^2 + 3U^2)] \quad (10)$$

Here we have assumed that $U \gg 1$.

The contraction predicted here is to be contrasted with the behavior seen for polymer brushes in good solvents.[20] There the layers seem to swell. This phenomenon may be explained by at least two theoretical mechanisms[18,21] and can be used in the design of novel microvalves.[22] The essential difference between the two systems lies in the incompressibility of the melt. In the good solvent brush the chains interact through a series of blobs, and when the layers are sheared the number of blobs increases and the layer swells.

One novel feature of the layer contraction considered here is that the dynamic modulus of the lamellae plays a significant role. For static lamellae this modulus is irrelevant, but for oscillatory shear it determines the deformation and hence the lamellar spacing.

III. Undulational Instabilities

The morphology considered above is that of the steady-state. We have said nothing so far about how it is achieved. For the lamellar size to change, chains must be exchanged between lamellae. This is a very slow process.[23-25] However, before the lamellae relax,

we expect an interesting effect to occur-namely, undulation of the layers perpendicular to both the shear and velocity direction. This undulation occurs because the lamellae in this regime are larger than their steady-state size under shear. By undulating, the layers effectively decrease their thickness. This instability is well-known for statically strained samples of classical smectics. For diblock lamellae under shear, however, the undulation should occur only in one direction, since in the other direction it would dramatically interfere with the flow.

This instability occurs when the strain is given by $|\epsilon| \approx 2\pi\lambda/D$. Here λ is the penetration length of the smectic. For an unsheared smectic, λ is comparable to the lamellar spacing. For a sheared smectic this will also be true, provided that the shear is weak. We describe the distortion of the local lamellar order by a variable[15,16] $u(x,y,z)$ that represents the displacement of a lamella from its equilibrium position in the z direction, which is defined to be normal to the layers. Simple geometric considerations relate $x = L/L_0$ to gradients of u:

$$x \simeq 1 + \frac{\partial u}{\partial z} - \frac{1}{2}(\nabla_\perp u)^2 \tag{11}$$

Here, $\nabla_\perp$ denotes the gradient in the $x-y$ plane. Thus, for $U \gg 1$ the free energy becomes

$$G \simeq \frac{\gamma}{L_0}\left[\frac{3}{2} - \frac{1}{2}\frac{S^2}{U} + \frac{S^2}{U^2}\epsilon + \frac{1}{2}\left(3 + \frac{S^2}{U^2}\right)\epsilon^2\right] + \frac{1}{2}K_1(\nabla_\perp^2 u)^2 \tag{12}$$

where

$$\epsilon = \frac{\partial u}{\partial z} - \frac{1}{2}(\nabla_\perp u)^2 \tag{13}$$

Within the Alexander–de Gennes approximation, the bending modulus is[26]

$$K_1 = {}^1/_3\gamma L_0 \tag{14}$$

By eq 12, the compression modulus is

$$\bar{B} = (3/L_0)\gamma \tag{15}$$

at zero shear.

For a sample confined between hard walls at $z = \pm D/2$, we consider the displacement field,

$$u = u_0 \cos(k_z z)\cos(k_\perp x), \tag{16}$$

where $k_z = \pi/D$. Within this single-mode approximation, the average free energy per unit volume can be expressed as

$$\langle G\rangle = \frac{\gamma}{L_0}\left[\frac{3}{2} - \frac{1}{2}\frac{S^2}{U} - \frac{S^2}{8U^2}u_0^{\,2}k_\perp^{\,2} + \left(\frac{3}{8} + \frac{S^2}{8U^2}\right)u_0^{\,2}k_z^{\,2}\right] + \frac{1}{8}K_1 k_\perp^{\,4}u_0^{\,2} \tag{17}$$

The optimal wavevector for undulations is given by

$$k_\perp^{\,2} = \frac{\gamma S^2}{2K_1 L_0 U^2} \tag{18}$$

The uniform lamellar phase is unstable to modulations above a critical shear stress given by

$$S_c^{\,2} = \sqrt{2}\pi\frac{U^2 L_0}{D} \tag{19}$$

Thus,

$$k_\perp^{\,2} \gtrsim \frac{1}{DL_0} \tag{20}$$

For shear stress near the critical value given by eq 19 the predicted wavelength of the undulation is of order $(DL_0)^{1/2}$. With increasing shear stress, the wavelength decreases as $1/S$.

IV. Conclusion

In this paper we have examined two important effects that can occur in well-ordered diblock copolymer melts under shear. The first, and simplest, is a change in the lamellar spacing, which always decreases. Shear can also drive a novel instability, i.e., the layers begin to undulate. This is analogous to the Helfrich–Hurault instability that is well-known for classical smectics.[15,16] However, in ordinary smectics it is usually driven by an applied tension perpendicular to the layers, or by an applied field. The smectic attempts to ease the effect of this tension by undulating in one or two dimensions. Here the mechanism is different. The shear decreases the "equilibrium" layer spacing, while the distance between the plates is fixed. The system undulates, but only does so in one direction. The undulational instability under shear relies on the coupling between shear and layer spacing that arises from chain elasticity and entanglements. These effects do not appear in the case of classical smectics. We note that the classical *tension-induced* Helfrich–Hurault effect is discussed in a recent study of smectic rubbers by Terentjev and Warner.[27] In that system the cross-links are permanent, and it is likely that a similar shear-induced undulation can also occur.

Here we have assumed a constant applied stress that creates a uniform strain across the sample. This should be valid for small applied stress. Above some critical applied stress interlayer sliding may occur and then only the stress on the upper and lower plates may be known. The strain may not be uniform, and because of interlayer sliding the stress on an individual layer may be a nonlinear function of the strain across the whole sample. The stress-strain relation between individual layers has been discussed by Joanny.[28] His calculation can be used to determine the stress on an individual layer due to a fixed applied strain across the entire sample. Other possible extensions of this work include the weak segregation limit, where it might be possible to solve the time-dependent equations of motion explicitly.

Note Added in Proof. More direct "field-induced"-type instabilities for diblocks in the cylindrical phase have been discussed: Williams, D. R. M. *Phys. Rev. E.* **1994**, *49*, R1811; and Hamley, I. W. *Phys. Rev. E.* **1994**, *50*, 2872. The classical Helfrich–Hurault instability for diblocks under strain in the lamellar phase is discussed by Wang: Wang, Z. G. *J. Chem. Phys.* **1994**, *100*, 2298.

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