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Equilibrium Surface Orientation of Lamellae

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ABSTRACT: We theoretically investigate the equilibrium orientation of lamellae arising from symmetric diblock copolymers in the presence of a hard wall. Firstly, the wall may preferentially wet with one of the species of the copolymer, thus favoring lamellar planes parallel to the wall. Secondly, chains are more easily stretched along the wall than they are in bulk; this favors the lamellar planes being perpendicular to the wall. Finally, the enhanced chain end density near the wall in the parallel orientation favors the planes flat along the wall. As molecular weight M approaches infinity, the most important effect is the wetting $\sim M^0$, followed by the nematic effect $\sim M^{-2/3}$, and lastly followed by the end effect $\sim M^{-8/9}$. In experimentally available copolymer domains, we find that the nematic and end effects have comparable magnitude. This magnitude appears more than adequate to influence the orientation of the lamellae. Lastly, we discuss effects of substrate roughness.

1. Introduction

Diblock copolymers, consisting of two distinct homopolymers joined end to end, can readily be made to phase separate, producing a variety of spatially periodic microphases.[1-4] When the two blocks of the polymer molecule (which we refer to as the A and B blocks) are symmetric in displaced volume in the melt state and have similar elastic properties, the only equilibrium structure available for the microphase is the lamellar structure. Additionally, if the molecules are very long, the lamellae will have the structure of the end-confined polymer brush: each block has one end confined in the plane of a lamella while the other end is stretched away from this surface. The theory of the brush state has been elucidated in refs 5 and 6, and the scaling laws predicted for the brush state have been verified for irreversible grafting of polymers onto a hard substrate.[7]

Typically, experimenters are able to observe lamellae formed by such copolymers by spin-coating a neutral surface (such as a silicon wafer) with a polymer + solvent droplet. As the solvent is gradually removed from the system, the copolymers spontaneously microphase separate. The orientation of the resulting lamellae can be observed through a variety of techniques.[8-11] These experiments suggest two possible orientations for lamellar planes near such a flat surface. If we let w stand for the normal direction to the wall and l stand for the normal direction to the lamellae, either $l \cdot w = 1$, with the lamellar planes *parallel* to the surface, or $l \cdot w = 0$, with the lamellar planes *perpendicular* to the surface, is observed. With the parallel orientation, interesting terracing of the lamellae is observed.[11] On the other hand, the perpendicular orientation forms distinctive striped patterns. There has been the suggestion that through annealing, the orientation can be changed.[9] Recently, Russell and co-workers have reported that both the parallel and the perpendicular orientations can obtain in their system of thin films of PS–PMMA on a gold substrate.[12] Thus, we investigate the factors contributing to the equilibrium orientation of diblock copolymer domains near a hard wall.

For either orientation, we may define an average interfacial free energy per unit area γ between the surface and the melt. This energy arises from the perturbation of fluid immediately adjacent to the wall. Three aspects of this boundary layer of fluid are significant.

The first and most obvious is the chemical composition. Other things being equal, the interfacial energy will be lower by some amount when, say, species A is adjacent to the wall rather than species B. In each orientation, we can define γ_W, the wetting contribution to the interfacial energy. Evidently this simple wetting effect favors the parallel configuration: $l \cdot w = 1$.

The second important feature is the state of chain tension in the boundary layer: is the fluid in the boundary layer under stress? In bulk lamellae, stress is stored in a spatially dependent manner: at the midplane interfaces the stress in the fluid vanishes, while it is a maximum in the vicinity of the A–B interfacial planes, where the chains are stretched maximally. In the configuration $l \cdot w = 1$ the fluid near the wall closely resembles the vicinity of a midplane interface: all of the chains are basically unstretched in the vicinity of the wall. In the configuration with $l \cdot w = 0$, chains are stretched out along the wall, and the wall samples alternatively regions of high stress (where A–B interfaces intersect the substrate) and regions of low stress (where midplane interfaces intersect the substrate). The stress stored by the fluid is smaller, however, than occurs in the bulk, because the presence of a hard flat wall cooperates with chain tension in producing chain extension. The wall induces a nematic ordering on nearby segments, causing them to lie in the plane of the wall, but otherwise disordered in their orientations. This nematic influence of the wall assists the creation of nematic order in the plane of the wall and thus cooperates with chain tensions. This lowering of stress can be interpreted as lowering the copolymer–substrate surface tension and thus favors the orientation $l \cdot w = 0$. The interfacial energy will thus have a part γ_n which depends upon the stretching of the chains at the wall.

Thirdly, the area density of free chain ends in the boundary layer can affect the interfacial energy. Calculations indicate that the molecular weight dependent interfacial energy between an unstructured melt and a neutral surface is given by $\gamma = \gamma_0 - A/M$, where A is some constant and M is molecular weight, when the interaction of the chain end groups is the same as that of interior monomers on the chain.[13,14] Simulations[15] and calculations[16] indicate that A is of the order kT for every end per unit surface within a monomer size of the interface. Thus, the presence of free ends produces an effect, γ_e. As end

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groups are highly concentrated at the free surface of a brush, we expect there to be many more free ends in the proximity of the surface in the parallel orientation than in the perpendicular orientation. Thus the third effect favors the parallel orientation.

Thus, $\gamma = \gamma_W + \gamma_n + \gamma_e$ in each orientation, representing the effect of block composition, the nematic effect due to chain stretching, and the effect of the chain end density at the surface. While γ may be large in either orientation, the *difference* between $\gamma^{\perp}$ and $\gamma^{\parallel}$ will determine the equilibrium configuration and will be controlled entirely by these three effects, in practice small. In the absence of kinetic effects, the system should choose the configuration with the smallest γ.

First, we consider the wetting effect, defining a dimensionless measure of the difference in interfacial energy between the substrate and the A and B fluids using the interfacial A–B tension for scale. Secondly, we consider how the nematic interaction between the wall with nearby chain segments cooperates with the chain tension in establishing the stretched-out chain configurations present in the lamellar phase. We will see that the nematic interaction can help chains stretching along the wall, but not chains running perpendicular to the wall. Thirdly, we calculate the end density in the limit of asymptotic strong stretching of the layer of fluid near the wall in the two orientations. Copolymers available today rarely exhibit the strong stretching we assume here; still, this calculation should give a good estimate of the order of magnitude of the effects. In the next section, we combine the results from the first three calculations in presenting a scaling form for the difference in interfacial free energy for the two lamellar orientations. In the Discussion section, we estimate the strength of these effects for the copolymers of ref 11, discuss the case of free surfaces, and consider the effect of surface roughness.

2. Differential Wetting

This effect is simply described: in the parallel case, the wall encounters only, say, A-block monomers. In the perpendicular case, the wall sees an equal number of both types of monomers. If the wall prefers to wet with either of the species, the parallel orientation will be selected. If we let γ_A stand for the interfacial energy between a dense liquid of infinitely long A-block homopolymer and the surface, and similarly for γ_B, then

$$\gamma_W^{\parallel} = \gamma_A \tag{1}$$

and

$$\gamma_W^{\perp} = {}^1/_2(\gamma_A + \gamma_B) = \gamma_A + W\gamma_{AB} \tag{2}$$

where we let $W \equiv {}^1/_2(\gamma_B - \gamma_A)$ in units of the interfacial tension, γ_{AB}, at the lamellar planes between the A and B blocks.

3. Nematic Interaction

Inevitably, a hard wall will serve to limit the conformations of Kuhn statistical segments near it. However, in the brush state, Kuhn segments are distorted because chains are stretched. The work per unit area required to insert a wall is altered by this stretching: we define the portion of this work arising from the stretching as γ_n.

The manner in which the wall and the chain stretching interact is easily described in the parallel orientation. The chain segments near the wall in the parallel orientation are far from A–B interfaces, residing at a distance h into the layer. Consequently, they are not stretched and are approximately ideal.[6] The presence of the wall, and a nematic interaction forcing monomers to lie along the wall when they are near it, thus has no effect on the state of tension. Evidently,

$$\gamma_n^{\parallel} \equiv 0 \tag{3}$$

The wall cannot affect the stretching of the chains in the parallel orientation.

However, in the perpendicular orientation, the chain segments are stretched out along the wall. Now the stretching of the chains affects monomers in contact with the wall. The elastic free energy per chain in the bulk is given by $F \approx (1/2)|h/R_z|^2$, where h is the layer height of one of the blocks (so that the repeat spacing between lamellar planes is $4h$) and R_z is the end-to-end distance in the z direction of the homopolymer constituents of the copolymer. Thus, the average elastic free energy density for bulk lamellae, f_b is given by

$$f_b = F/V \tag{4}$$

where V is the displaced volume per chain in the melt. Now consider a segment of chain of volume Δv and lateral extent Δz along the lamellar normal. For the sake of generality, we assume that this chain segment lives in a d-dimensional space which includes the lamellar normal direction, z. Then the elastic free energy of this segment, ΔF, is given by

$$\Delta F = \frac{1}{2}\left|\frac{\Delta z}{\Delta R_z}\right|^2 \tag{5}$$

with $\Delta R_z^2 = \Delta v/(ad)$, the squared end-to-end distance of the segment, and a is the packing length of the polymer. Thus, $\Delta F \sim d$ everywhere throughout the layer. In the bulk, we should pick $d = 3$, but if the segment is near the surface, then we must choose $d = 2$, thus lowering the elastic energy of all segments near the wall by a factor of ${}^2/_3$. The elastic energy density of the layer of fluid near the wall is less than the elastic energy density in the bulk. The range of this effect must be on the order of a, so we find that the effect of the wall can be interpreted as lowering the free energy of the system by $({}^1/_3 f_b)a$ for each unit of wall area. We interpret this effect as $\gamma_n^{\perp}$:

$$\gamma_n^{\perp} \approx -\frac{1}{3}af_b \approx -\frac{a}{V}\left|\frac{h}{R_z}\right|^2 \tag{6}$$

Of course, there must be a smooth crossover from two-dimensional behavior near the wall, but this can only change the result by a factor of order unity.

4. Chain Ends

We must calculate the surface density of free ends within a monomer's length of the wall, keeping in mind that each end lowers the free energy of the polymer–wall interface by about kT.

The concentration of free ends is hardly uniform in the bulk lamellar phase; the concentration becomes modulated in the direction of the lamellar normal. Ends are expelled from the vicinity of the A–B interface planes and congregate near the midplane interfaces. Neglecting the possibility of midplane interpenetration and assuming that the free energy per copolymer block, $F \approx |h/R_z|^2$, is indefinitely greater than kT, it is possible to calculate the end density per unit distance from the A–B interfaces $\epsilon(z)$ as[6]

$$\epsilon(z) = \frac{1}{V}\frac{z}{(h^2 - z^2)^{1/2}} \tag{7}$$

where V is the displaced volumer per copolymer block in the melt and z is the distance to the nearest A–B interfacial plane. Note that the end density in this case actually diverges at $z = h$ (the midplanes) and vanishes at $z = 0$ (the A–B interface).

It should be kept in mind that neither the large F (and hence strong stretch) nor the no-interpenetration assumption is achieved in practice. As far as the asymptotic strong stretching assumption is concerned, we nevertheless feel that our calculation can provide excellent insight into the qualitative features of the end effect as it applies to readily available copolymers. On the other hand, the interpenetration of adjacent polymer brushes is considered in ref 18 and indeed must represent the case of bulk lamellae. We follow their analysis.

The authors of ref 18 estimate an interpenetration length scale, ξ. By considering chains with their free ends near an A–A interface, one can ask how far a chain can penetrate into an adjacent layer at a free energy cost of no more than kT. We quote their result:

$$\frac{\xi}{h} \approx \left(\frac{h}{R_z}\right)^{-4/3} \qquad (8)$$

Within $\pm\xi$ of a midplane interface, eq 7 is no longer applicable; the effect of interpenetration is to cut off the singularity present at $z = h$ in eq 7. In fact, $\epsilon(z)$ must approach a constant as $z \rightarrow h$; this constant is given by eq 7 with $z = h - \xi$:

$$\epsilon(z) \approx \epsilon(h - \xi) = \frac{1}{V}\left(\frac{h}{\xi}\right)^{1/2} \qquad (9)$$

for all z with $(h - \xi < z < h)$, as per Figure 1. If we recall that the bulk density of free ends is given simply by $\epsilon_b = 1/V$, as each copolymer block contains a single end in a volume of V, then we find an enhancement of end concentration at the midplanes, ϵ_{A-A}, of

$$\epsilon_{A-A} = \epsilon_b\left(\frac{h}{\xi}\right)^{1/2} \qquad (10)$$

This represents a considerable enhancement of the midplane end density.

We note that if a neutral wall were inserted into a bulk phase of lamellae, the end density the wall sees will depend greatly upon the orientation of the wall. If the wall cuts the lamellar planes, the density of ends at the wall will be modulated along the wall, but the average end density along the wall will be only the bulk value. On the other hand, if the wall is inserted between an A–A midplane, the density is not modulated along the wall and maintains its maximal value.

We now consider the possibility that the wall might alter the structure of the fluid near it so that all similarity to the unperturbed lamellar phase is lost. Fortunately, when the wall is placed along a symmetry plane of the lamellae, we can be confident that the wall–polymer boundary layer does not alter quantities such as the end density, by adapting some arguments of Silberberg.[17] In the early eighties, he developed a symmetry scheme which he calls "segment swapping", in which the structure of a melt in the vicinity of a neutral wall is deduced. An infinite melt is cut by an imaginary plane. Any chain configuration crossing this plane is accompanied, at least statistically, by a mirror image chain configuration. Each chain trajectory traversing the fictional wall can be made to "bounce" off the wall by reconnecting a configuration and its mirror image, as in Figure 2. Thus, two new chain configurations are produced; one lies entirely to the left of the fictional wall, and the other is entirely on the right. Silberberg assigns these new wall-respecting trajectories the combined statistical weights of all configurations leading to them, so that the only free energy cost of the whole process is due to the decrease in orientational entropy of chain segments at the wall in order to keep them from crossing. Now, the right half of the system can be dispensed with and replaced with a real wall. In particular, Silberberg showed that the density of free ends as a function of position from the wall is exactly that present before the segment swapping operation has been performed and the wall inserted, at least in the unstructured melt.

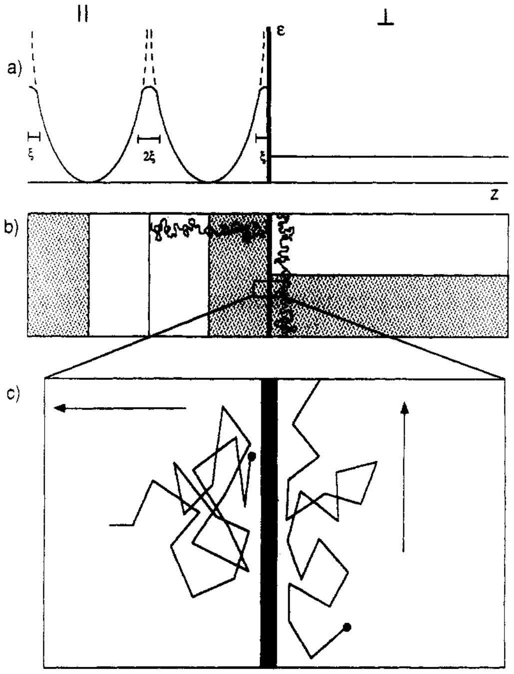

Figure 1. End density vs height. (a) Here we show schematically the end density as a function of distance from the wall for the two orientations: on the left is shown the end density in the parallel orientation. The density does not diverge at the lamellar midplanes, nor at the wall, yet is greatly enhanced over that found in the perpendicular orientation, shown on the right portion of the graph. (b) Here we show schematically the orientation of the lamellar planes and typical chain orientations in the layer. All chains in the parallel orientation are nearly ideal as they encounter the wall, while in the perpendicular orientation the chains run along the wall and are stretched locally. (c) Here we show schematically the vicinity of the wall. The arrows indicate the direction of the chain tension. In the parallel case, the tension cannot cooperate with the nematic ordering induced by the wall, while in the perpendicular case, the tension and nematic order assist each other in determining chain configurations.

The application of this argument to the relationship of the A–A midplanes and the vicinity of the wall is now apparent. The key element in the argument is that the fictional wall be placed in a position of symmetry: chains and mirror image chains must have the same statistical weights. But, this is precisely the situation for only two possible wall orientations: the parallel and perpendicular orientations we consider here.

In the parallel case, the vicinity of the wall resembles an A–A midplane, and the end density is given by ϵ_{A-A}. Each end within a monomer's length, which we take to be the packing length, a, acquires and entropic bonus of order kT: thus we find that

$$\gamma_e^{\parallel} = -\frac{a}{V}\left(\frac{h}{\xi}\right)^{1/2} \qquad (11)$$

In the perpendicular orientation, the wall end density is

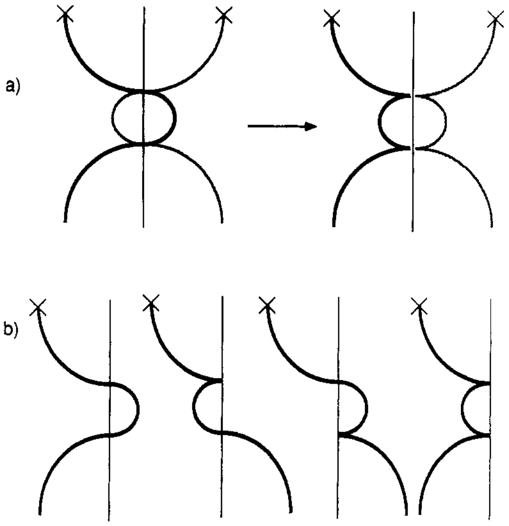

Figure 2. Segment swapping. (a) A chain configuration and its mirror image are shown here in the vicinty of an A–A interface. The crosses indicate the portion of the chain which stretches away to the A–B interface, far away into the layer, and the unmarked ends are free. By reconnecting the statistically identical chain configurations, two new configurations are produced which respect the A–A midplane, at a free energy cost of orienting the chain segments actually at the wall. (b) Here we show all of the chain configurations which lead to the same wall-respecting configuration. The first three cannot occur in the presence of the wall, but the Silberberg prescription allots the fourth configuration the statistical weights of all four of these configurations. We see that the position of the physical chain end has the same weight to be in this position as in the case of no wall, i.e., an A–A midplane interface.

ϵ_b, so that

$$\gamma_e^{\perp} = -\frac{a}{V} \qquad (12)$$

This effect, considered alone, greatly favors the parallel orientation.

5. Comparison

We are now in a position to estimate the surface tension between the copolymer droplet and the hard wall as a function of the orientation of the lamellae. The work per unit area required to change the orientation from the perpendicular to the parallel one is evidently given by $\Delta \equiv \gamma^{\parallel} - \gamma^{\perp}$. The wetting contribution, Δ_W may be expressed as

$$\Delta_W = -W\gamma_{AB} \approx -c_w'\frac{a}{V}V^{-1} \qquad (13)$$

where we note that $\Delta < 0$ favors the parallel orientation, and we display the form of Δ_W in the scaling limit, $V \rightarrow \infty$. The nematic contribution Δ_n has the form

$$\Delta_n = +c_n\frac{a}{V}\left|\frac{h}{R_z}\right|^2 \approx +c_n'\frac{a}{V}V^{1/3} \qquad (14)$$

where we use $h \sim V^{2/3}$ appropriate for lamellae arising from diblock copolymers in the strong segregation limit. Finally, we find that Δ_e has

$$\Delta_e = c_e\frac{a}{V}\left[1 - \left(\frac{h}{\xi}\right)^{1/2}\right] \approx -c_e'\frac{a}{V}V^{1/9} \qquad (15)$$

Combining these contributions,

$$\Delta \equiv \Delta_W + \Delta_n + \Delta_e = \frac{a}{V}\left[-W\gamma_{AB}\frac{V}{a} + c_n\left|\frac{h}{R_z}\right|^2 + c_e\left(1 - \left(\frac{h}{\xi}\right)^{1/2}\right)\right] \qquad (16)$$

where c_n and c_e are positive constants of order unity. The scale we have chosen for Δ is $a/V \approx 1/R_z^2$. As $V \rightarrow \infty$, we find that

$$\Delta = \frac{a}{V}[-c_w'V^1 + c_n'V^{1/3} - c_e'V^{1/9}] \qquad (17)$$

Eventually, the c_W' term dominates, and the parallel orientation is favored. But, for any finite V there is a range of W near zero where the nematic and end effects dominate.

6. Discussion

It is instructive to estimate the size of these three effects for actually occurring diblock copolymer systems. For instance, the authors of ref 11 investigated several PS–PMMA copolymers. The average molecular weight of each block was ~50 000 amu, and therefore they had a displaced volume of 10^5 Å^3, as the mass density of the copolymer is ~1 g/cm^3. Therefore, we calculate that $R_z^2 = V/2a \approx 5 \times 10^3$ Å^2, where we use $a \sim 10$ Å.

The authors of ref 11 report an average repeat spacing of ~450 Å as determined by optical interference microscopy, so that $h/R_z \sim 1.5$. Thus, the Δ_n part of eq 16 contributes approximately $+2\,kT/R_z^2$. Likewise, we find that Δ_e in eq 16 contributes $(-1/3\,kT)/R_z^2$ to the difference in surface tensions. Now we can estimate a lower bound on the dimensionless quantity W: W must be strong enough to force the lamellae to adopt the parallel configuration that the authors of ref 11 observed. Thus, we infer that $W\gamma_{AB}$ must be at least the order of $1.6\,kT/R_z^2$. The interfacial tension at the lamellae planes, γ_{AB}, is given by the total free energy per chain (which scales like the elastic energy per chain) per area occupied by each chain, V/h:

$$\gamma_{AB} \approx \frac{h}{V}\frac{h^2}{R_g^{\,2}} = \frac{a}{V}\left[\frac{h}{a}\frac{h^2}{R_z^{\,2}}\right] \qquad (18)$$

Thus, we estimate that in this case $\gamma_{AB} \sim 25a/V$. Thus, $W > 0.04$, in order to force the parallel orientation. Of course, it is likely that W is much larger in this case, as the authors were attempting to make a study of terracing at the top of a thin layer of the parallel orientation.

This analysis should apply equally well to the flat interface of a copolymer droplet and air. The nematic effect arises because of the flat nature of the interface; at a polymer–air interface this constraint on segment orientation still operates. Likewise, free ends gain their bonus of kT only through their ability to pack more easily in the constrained layer next to the wall than interior monomers. As long as the boundary between polymer and air is sharp enough (on the scale of a), ends will continue to operate in this way. The polymer–air interface will in general have its own effective W. In the preparation of thin films, there should exist a competition between the substrate W and the air W.

With thin films, it is entirely possible that the free surface and the interface with the hard substrate may prefer different orientations. We do not have much to say about how, say, a perpendicular configuration could fuse into a parallel one only a few layers away: all of our reference states are uniform. However, if the difference in the γ's for the two surfaces is smaller than γ_{AB}, then there will not be enough free energy in the system to significantly distort the lamellar structure of the domains. We would thus expect a single configuration throughout the entire thin film.

Nevertheless, it is clear that in order to observe the effects of the nematic and end effects, W should be made as small as possible. It should be possible to tune the W

for the substrate by altering it chemically, while the effective W for air could be tuned by tailoring the copolymers involved.

Thus far, we have neglected the effect of surface roughness on the equilibrium orientation of the lamellar domains. We can define $\gamma_r^{\parallel}$ and $\gamma_r^{\perp}$ as the contribution to the polymer–wall interfacial energy arising from the distortion of the lamellar domains as a result of the roughness of the wall. In either orientation, γ_r can be large (up to $\sim \gamma_{AB}$), but we expect that $\gamma_r^{\parallel} \sim \gamma_r^{\perp}$ in any event. Still, Δ_r can be large, and its sign depends on the exact constant of proportionality between $\gamma_r^{\parallel}$ and $\gamma_r^{\perp}$, the estimation of which is a delicate and difficult task which we do not address here. We can estimate, however, the scale of roughness at which γ_r becomes comparable to the terms we find in Δ above. When $\gamma_r \ll |\Delta|$, we can be confident that our flat wall calculations are applicable.

Suppose the wall is rippled sinusoidally in one direction with amplitude η and wavevector q, and further that the lamellae are oriented parallel to the wall. When $\eta \ll q$, it is possible to calculate using ref 19 how far the sinusoidal distortion penetrates the copolymer layer in the Alexander–de Gennes model.[20,21] If we let M stand for the number of affected layers, it is found that $M \sim (qh)^{-2}$. In order to heal the distortion in M layers, each chain in the distorted layer is stretched or compressed by a distance on the order of η/M, resulting in M free energy costs of magnitude $\eta^2 M^{-2} R_z^{-2}$ for each copolymer molecule encountering the wall. There are h/V such copolymers per unit wall area: we thus interpret this cost as $\gamma_r^{\parallel}$:

$$\gamma_r^{\parallel} \approx + \frac{h}{V} \frac{\eta^2 q^2 h^2}{R_z^{\;2}} \approx \gamma_{AB} (q\eta)^2 \tag{19}$$

For the copolymers of ref 11, we estimated that $\gamma_{AB} \approx 25a/V$. We wish to make γ_r much smaller than any component of Δ, i.e., much smaller than a/V. Thus, if we impose that the substrate satisfies $q\eta \ll 0.2$, then we can be confident that the rippling of the surface is unimportant for these copolymers.

Of course, substrates likely to be used experimentally probably will not display the corrugated roughness considered above. In general, the surface profile will vary isotropically rather than in just one direction along the wall. The appearance of roughness in two directions rather than one can only modify the prefactors we omitted from our discussion.

However, if the roughness *is* translationally invariant in, say, the x direction, the mean wall normal is no longer the only direction the lamellar domains are aware of. There are now two distinguishable orientations with $w \cdot l = 0$: one has $l \parallel x$ (the *perpendicular-1* orientation), and the other has $l \parallel y$ (the *perpendicular-2* orientation). For the perpendicular-2 orientation, we may consider what wall shapes are symmetries of the chain configurations: only a flat wall will do. If the wall curves, the chains also must run along this curving surface. Thus, the perpendicular-2 orientation is accompanied by a possibly large $\gamma_r^{\perp 2}$, as above.

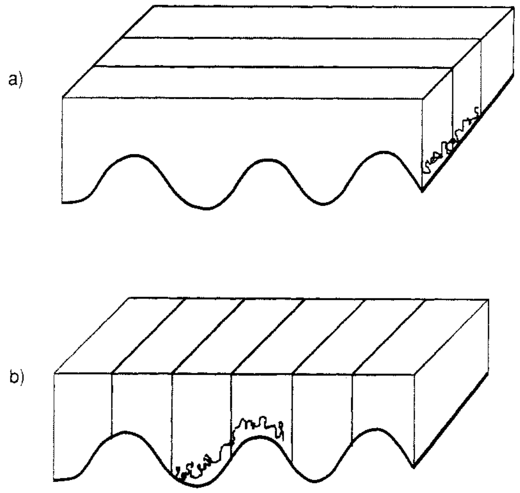

Figure 3. Two perpendicular orientations. When the surface is rough in only one dimension, two orientations with $l \cdot w = 0$ are possible. (a) In the perpendicular-1 orientation, the lamellar normal is oriented parallel to the only remaining "smooth" direction. Chain trajectories are not affected greatly, as the wall is still a local spatial symmetry of chain configurations. (b) In the perpendicular-2 orientation, the lamellar planes are aligned in the "rough" direction, and the chains must distort in order to follow the contour of the wall.

On the other hand, we consider the perpendicular-1 orientation. Here, the chains can sample the curvature of the surface only through their lateral dimensions in the lamellar planes, as shown in Figure 3. As long as the surface does not curve too greatly over this lateral excursion distance ($\sim R_g$, the radius of gyration of the copolymer block), the wall is an approximate local symmetry of the chain configurations. The chains can run along a flat surface. As the maximal radius of curvature of the undulating surface, R_0, is $(\eta q^2)^{-1}$, we arrive at the following criterion which ensures that $\gamma_r^{\perp 1} \approx 0$:

$$R_g \ll R_0 \rightarrow (\eta q)^2 \ll q^{-2} \frac{a}{V} \tag{20}$$

We can pick (ηq) large enough to rule out the formation of either the parallel or perpendicular-2 orientations and still have a small deformation cost to form the perpendicular-1 orientation by picking q sufficiently small. By suitably scoring a substrate, one could thus hope to achieve controlled global order in the lamellae.

7. Conclusion

In the scaling limit $V \rightarrow \infty$, the parallel orientation is heavily favored for any finite differential wetting W. For sufficiently small values of W, however, we find that the perpendicular orientation should be favored due to the nematic effect. At smaller V, the nematic effect and the end effect become competitive, and the equilibrium orientation may well become the parallel one again.

The size of the effect should be emphasized. Each effect separately is capable of producing energies of the order kT in a wall surface area of R_z^2. This represents a much larger free energy than is available from the fluctuations of lamellar orientations activated thermally, usually kT per several h^2. Thus, we feel that we have identified the most dramatic equilibrium effects. Surface roughness plays an important role in determining lamellar orientations, as noted above. Kinetic effects not considered here may be very important, as well.

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