Smectic Rod−Coil Melts Confined between Flat Plates: Monolayer−Bilayer and Parallel−Perpendicular Transitions

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ABSTRACT: We study theoretically the equilibrium properties of a rod−coil diblock copolymer melt confined between two flat plates. We assume that the system forms lamellae in the bulk. The plates may have a preference for either the rods or coils. We investigate whether the preferred alignment of the lamellae is parallel or perpendicular to the plates and how the lamellar spacing changes compared to the bulk lamellar spacing. We find that this system is much more constrained than the analogous coil−coil system and for certain values of the rod−coil interfacial tensions that perpendicular lamellae exist for quite thick films. For dissimilar bounding plates we find the antisymmetric parallel morphology may exist.

1. Introduction

Rod−coil block copolymers consist of a flexible coil polymer irreversibly joined to an inflexible rodlike polymer. These types of polymers have attracted increasing interest recently, both experimentally[1−5] and theoretically.[6−9] In the strong-segregation limit, which we focus this study on, melts of these diblocks form a variety of novel phases,[5] quite different from the analogous coil−coil systems.[10] The main reason for this is that the inflexibility of the rodblocks makes this system quite different from coil−coil systems. Although the rod−coil diblock melts do still microphase separate, some of the more novel phases that have been predicted and observed are pancakelike micelles and mushroomlike micelles. In this study we shall concentrate on rod−coil melts whose bulk morphology is a lamellar phase.[5,6,8]

Another recent problem of interest in polymer physics is the equilibrium properties of thin, confined diblock (coil−coil) copolymer melts.[11−13] In this problem a diblock melt is confined between two flat, infinite plates which may prefer one of the blocks. The presence of the two plates inhibits the formation of islands and holes,[11] which may form for a thin melt sample bounded by a free surface. Thus, if the thickness of the thin film is not exactly an integer multiple of the bulk lamellar spacing, the lamellae cannot achieve their bulk equilibrium spacing. This leads to the possibility of two different orientations of the lamellae, with respect to the plates,[12] as well as a change in the lamellar spacing,[11] compared to the bulk lamellar spacing. The optimal spacing of the lamellae under the constraint of fixed film thickness is determined by minimization of the free energy over the number of lamellae in a parallel orientation and comparison with the free energy of the perpendicular orientation.

In this paper we combine these two threads to study the thin film behavior of a rod−coil copolymer melt when confined between two flat plates. The system shows some quite novel behavior, compared to the analogous coil−coil system. For example, because the rods cannot stretch, our system is much more constrained than the coil−coil system. As a result, in certain circumstances, we find a number of parallel to perpendicular transitions, as the film thickness is increased. In section 2 we begin by discussing the bulk behavior of these rod−coil melts. One interesting point we find is that, for all values of the rod−coil interfacial tension (in the strong segregation limit), the so-called bilayer phase always has a free energy lower than or equal to that of the monolayer phase. This is compared to Semenov's study[8] where he finds that for certain values of the rod−coil interfacial tension the monolayer phase has a lower free energy than the bilayer phase. In section 3 we present the equilibrium free energy models for a number of possible morphologies for thin film rod−coil melts. In section 4 we derive the phase diagram for this system under a variety of plate/polymer interfacial energies. In section 5 we present our conclusions.

2. Bulk Behavior

We consider a melt of rod−coil diblocks with the rods having length L and cross-sectional area d^2 where $d \ll L$. The flexible parts of the diblocks are considered to have N segments (monomers) of size a. In accordance with previous work[6−9] on rod−coil melts, we define the following dimensionless parameters

$$\lambda = \frac{Na^3}{Ld^2} = \frac{\phi}{1-\phi} \tag{1}$$

$$\kappa = Na^2/L^2 \tag{2}$$

and

$$\nu = \kappa/\lambda \tag{3}$$

where ϕ is the volume fraction occupied by the chains. Thus, λ represents the ratio of the chain volume fraction to the rod volume fraction. Semenov and Vasilenko[6]

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show that ν is proportional to the ratio of chain persistence length to rod persistence length and so $\nu \ll 1$. These rod−coil melts are theoretically predicted to form lamellar[6,8] and hockey-puck-type[9] phases, and experimentally, mushroom-type micelles[5] and zigzag phases[3] have also been observed. We limit ourselves here to the lamellar phase where layers of rods and coils alternate. There are two types of lamellar phases that may occur in a bulk melt. Semenov and Vasilenko refer to them as a monolayer phase and a bilayer phase. The monolayer phase has less stretching energy per molecule, while the bilayer phase, which is similar to the lamellar phase of the usual coil−coil diblock melt, has less interfacial energy per molecule. These phases are smectic, and so they are denoted[8] Sm A_1 and Sm A_2 in this paper. This notation is employed because the rods are perpendicular to the rod−coil interface. In general, the rods do not have to be perpendicular to the rod−coil interface; i.e., they may tilt at some constant angle. The tilted phase arising from monolayers is referred to as a Sm C_1 phase, while the tilted phase arising from bilayers is referred to as Sm C_2. The free energy of these phases can be simply determined as the sum of the elastic stretching energy of the coils and the interfacial energy at the rod−coil interface. We shall closely follow the theoretical model proposed in Semenov's pioneering works.[6,8] The elastic energy is proportional to k_BTx^2/Na^2, where T is the temperature and x is the distance the coil is stretched through, while the interfacial energy is $A\gamma_{RC}$, where A is the rod−coil interfacial area and γ_{RC} is the rod−coil interfacial tension. Thus, the dimensionless free energy, F_1, per molecule of the monolayer system is

$$F_1 = \frac{F_{el} + F_{int}}{\gamma_{RC}d^2} = \frac{\lambda}{16\nu g_{RC}} \cos^2 \tau + \frac{2}{\cos \tau} \qquad (4)$$

where τ is the angle of tilt of the rods with respect to the lamellar normal and $g_{RC} \equiv \gamma_{RC}d^2/k_BT$. g_{RC} is thus a dimensionless measure of the rod−coil surface tension. For the Sm A_1 phase, $\tau = 0$, while for Sm C_1, $0 < \tau < \pi/2$. The repeat unit size of one lamella is $L(1 + \lambda) \cos \tau$. The bilayer phase is different from the monolayer phase because coils now stretch double the distance. This results in a multiplicative factor of 4 for the stretching energy (compared with the monolayer stretching energy). However, this is compensated by a reduction in the interfacial energy because each coil now only has an interface with one rod. Thus, the interfacial energy decreases by a factor of 2. Thus, for the bilayer system the dimensionless free energy, F_2, per molecule is

$$F_2 = \frac{F_{el} + F_{int}}{\gamma_{RC}d^2} = \frac{\lambda}{4\nu g_{RC}} \cos^2 \theta + \frac{1}{\cos \theta} \qquad (5)$$

Here $\theta = 0$ corresponds to the Sm A_2 phase, while for Sm C_2, $0 < \theta < \pi/2$. The repeat unit size of one lamella is $2L/(1 + \lambda) \cos \theta$. Note in writing these equations for the free energies; we follow Semenov's[8] argument that the interfaces between lamellae are irregular and so the interfacial energy varies as $1/\cos \theta$ rather than Halperin's[7] argument which implies the interfacial energy varies as $1 + \tan \theta$.

To obtain the actual observed (bulk) system, one minimizes F_1 and F_2 with respect to θ. This gives an optimal tilt angle for any value of g_{RC}. For Sm C_1 this angle is given by $\cos \tau_b = 2(2g_{RC}\nu/\lambda)^{1/3}$ while for Sm C_2 it is $\cos \theta_b = (2g_{RC}\nu/\lambda)^{1/3}$. Substituting these optimal angles back into the free energy expressions (4) and (5) gives $F_1^{min} = 2^{-4/3}3(\lambda/\nu g_{RC})^{1/3}$ while $F_2^{min} = 2^{-4/3}3(\lambda/\nu g_{RC})^{1/3}$. As g_{RC} increases, one should find a number of phase transitions between various phases.[8] At very low g_{RC}, i.e., $g_{RC} \approx 0.01(\lambda/\nu)$, the system forms a disordered nematic phase. Interestingly, for $g_{RC} \leq 0.0625(\lambda/\nu)$ the two types of phases (monolayers and bilayers) have exactly the same free energy, and their tilt angles are simply related by $\cos \tau_b = 2 \cos \theta_b$. Thus, in this region these two phases would have exactly the same lamellar spacing, the only way to differentiate between the two experimentally would be to possibly look at the tilt angle of the rods. Of course, this result has built in it a number of approximations, and thus a more rigorous analysis which includes the effects of steric interactions between rods favors monolayers over bilayers.[14] We do not use such rigorous models[14] here, because this is the first study of a complex system, and such rigorous models would obscure the main physics of the system. For $0.0625(\lambda/\nu) < g_{RC} < 0.5(\lambda/\nu)$, the Sm C_2 phase has the lowest free energy, while for $g_{RC} \geq 0.5(\lambda/\nu)$, we obtain the Sm A_2 phase.

3. Confined Thin Film−Free Energy Model

We now consider the case where the rod−coil copolymer melt is confined between flat plates. The plates are considered to lie in the $x-y$ plane, with length Ω_x in the x direction and length Ω_y in the y direction. For our purposes we consider Ω_x and Ω_y to be very large, effectively infinite. The diblock sample is confined between the two plates which have a separation H in the z direction. We limit the discussion to the strong-segregation limit, i.e., $g_{RC} \gtrsim 0.0625(\lambda/\nu)$. In the case of a confined thin film, we must also consider a polymer−plate interfacial energy term. When the coil blocks are next to the plates, this interfacial energy term is simply of the form $A\gamma_{CP}$, where A is the coil−plate surface area and γ_{CP} is the coil−plate interfacial tension. For the case where the rods are next to the plates, this term is not as simple because both the rods and plates are solid and so do not deform as the rods tilt. If we were to assume the rods have a regular, uniform cross section, the tilting implies an interfacial energy penalty term of the form $A\gamma_{RP}[1 + \tan \psi] \cos \psi$, where γ_{RP} is the rod−plate interfacial tension and ψ is the angle between the tilted rods and the unit normal to the plates. However, this expression does not behave well for small ψ; i.e., it varies such as $1 + \psi$, which is not typical of smectic fluids.[15] Thus, we write for the rod−plate interfacial energy $F_{rod-plate} = A\gamma_{RP}[1 + 2(1/\cos \psi - 1)] \cos \psi$, where ψ is the tilt angle of the rods adjacent to the plates and γ_{RP} is the rod−plate interfacial tension. This expression can be simplified to $F_{rod-plate} = A\gamma_{RP}(2 - \cos \psi)$ and has the property that for small tilts the interfacial energy varies as $1 + \psi^2/2$, which is the usual form for similar type smectic fluid problems[15] and is of a similar nature to the approximation for the rod−coil interfacial area in the bulk Sm C_2 phase.[8]

We now write down the free energy of the system. Note we do not consider the Frank bend, splay, and twist free energies[15] here because all rods are essentially aligned parallel and coplanar. Thus, such terms would be negligible. If the rods are preferred at the plates, the rods must be in a bilayer-type configuration in the layer adjacent to the plates. In the interior region, the

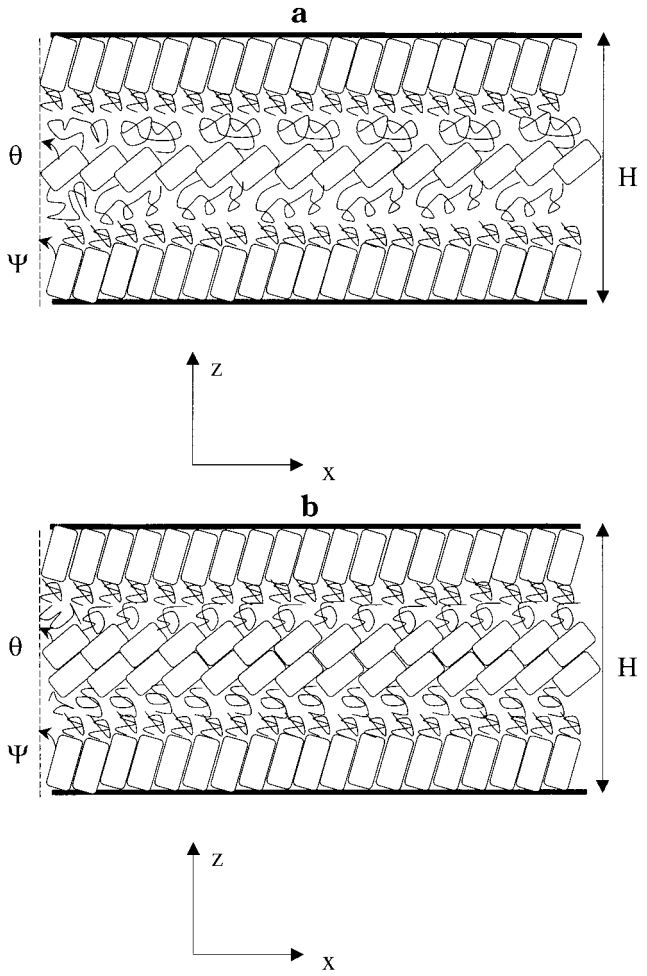

Figure 1. Thin film parallel lamellae configuration with rods at both plates (symmetric configuration): (a) Sm A_1 or Sm C_1 in the interior; (b) Sm A_2 or Sm C_2 in the interior.

configuration may be either a monolayer type or bilayer type (see Figure 1). We do not assume the tilt angle of the rods at the plates is the same as the tilt angle of rods in the interior but rather write down the free energy of the system as a function of these two tilt angles. Consider first a Sm A_1/Sm C_1 state in which the lamellae form parallel to the confining plates. The dimensionless free energy, $F_{1,||} \equiv F/(\gamma_{RC}\Omega_x\Omega_y)$, of this state is

$$F_{1,||} = \left[\frac{\lambda}{16\nu g_{RC}}\cos^3\theta + 2\right]n_m + \beta(i)\left[\frac{\lambda}{4\nu g_{RC}}\cos^3\psi + 1\right] + f_{surface}(i) \quad (6)$$

where $i = 1$ corresponds to rods at both plates, $i = 2$ corresponds to rods at one plate and coils at the other, and $i = 3$ corresponds to coils at both plates. Now, when

$$i = 1, \quad \beta(i) = 2 \quad \text{and} \quad f_{surface}(i) = 2\Gamma(2 - \cos\psi)$$

$$i = 2, \quad \beta(i) = 1 \quad \text{and} \quad f_{surface}(i) = \Gamma(2 - \cos\psi) + \Gamma + \delta$$

$$i = 3, \quad \beta(i) = 0 \quad \text{and} \quad f_{surface}(i) = 2(\Gamma + \delta) \quad (7)$$

Here we have defined a surface tension ratio, $\Gamma \equiv \gamma_{RP}/\gamma_{RC}$, and a surface tension difference, $\delta \equiv (\gamma_{CP} - \gamma_{RP})/\gamma_{RC}$. In eq 6 n_m denotes the number of monolayers that may fit in the interior region $H - \beta(i)\, L(1 + \lambda)\cos\psi$. The minimum number of lamellae that can fit into this region is n_m^*, which corresponds to the case where the rods have no tilt and the lamellar spacing is $L(1 + \lambda)$. If we measure lengths with respect to $L_0 = 2L(1 + \lambda)\cos\theta_b$, this implies $n_m^* = \mathrm{INT}[2H\cos\theta_b - \beta(i)\cos\psi]$, where INT[ ] denotes the smallest integer greater than or equal to the number in the square brackets and $H \equiv H/L_0$. Note that $n_m = n_m^*, n_m^* + 1, n_m^* + 2, \ldots$ and $n_m^* \in I$ (i.e., a positive integer).

Next consider determining the free energy of the Sm A_2/Sm C_2 states. Again we do not assume the tilt angle of rods adjacent to the plates is the same as rods in the interior. Thus, the dimensionless free energy, $F_{2,||}$, for this state is

$$F_{2,||} = \left[\frac{\lambda}{2\nu g_{RC}}\cos^3\theta + 2\right]n_b + \beta(i)\left[\frac{\lambda}{4\nu g_{RC}}\cos^3\psi + 1\right] + f_{surface}(i) \quad (8)$$

where $\beta(i)$ and $f_{surface}(i)$ are defined as in eq 7 and n_b is the number of bilayers in the interior region. Once again, we denote the minimum number of bilayers that fits into this region by n_b^* and $n_b^* = \mathrm{INT}[H\cos\theta_b - (1/2)\beta(i)\cos\psi]$. For both symmetric (rods at both plates or coils at both plates) and antisymmetric configurations, $n_b^* \in I$, and so $n_b = n_b^*, n_b^* + 1, n_b^* + 2, \ldots$.

The above two expressions for the free energy of lamellae parallel to the confining plates must be minimized over both θ and ψ subject to the restrictions on the layer numbers. As far as the polymer−polymer interactions are concerned, both θ and ψ would like to be close to θ_b. However, because the film has a finite thickness, this cannot be satisfied for all H. As far as the polymer−plate interaction is concerned, if rods are preferred, ψ should preferably be zero, and so the rod−plate area is minimized. Thus, a nonzero ψ increases the term $f_{surface}(i)$. The problem of minimizing the system's free energy is more complicated than the analogous problem for coil−coil systems.[11,12] In that case, for a particular thickness, the free energy only had to be minimized between two possible states (symmetric and antisymmetric). In our case we must minimize over two angles, over monolayer and bilayer configurations, and also over symmetric and antisymmetric states. Thus, analytic formulas for transitions from states with different layer numbers are difficult to obtain. Here we do the minimization numerically. When this is done, one obtains the optimal configuration of the lamellae in the parallel orientation, i.e., the parallel configuration which has the minimum free energy.

So far our discussion has been restricted to parallel orientation of the lamellae with respect to the confining plates. In principle, the system may be able to lower its free energy via a variety of other types of morphologies. For example, the lamellae may orient perpendicular to the plates and in doing so they can obtain their bulk spacing, at the cost of rod−plate interfacial energy. It is also possible that the morphology of the system could be a mixed type[13,16−19] with both parallel and perpendicular alignment. Matsen has recently shown that these types of morphologies for coil−coil diblocks on homogeneous surfaces are only partially stable. Other more exotic morphologies or undulations of the interface

may also be possible. In particular, undulations of the interface (due to the Helfrich−Hurault effect[15]) occur for lamellae (and smectics in general) under compression. Because this is a first study of this system, we shall not address this morphology here, because the physics for such a morphology is quite complex because of the additional possible bend and splay terms. However, we feel the extra free energy terms for such a morphology might be quite large and so not comparable to the free energy of the present morphologies. In any case, such a calculation is left to future work. We shall, however, concentrate here on perpendicular lamellae. Walton et al.[12] showed that in the coil−coil system such perpendicular lamellae occurred primarily for ultrathin films, i.e., less than a monolayer thick.

In the perpendicular morphology, because we consider the plates to be essentially infinite, the lamellae may achieve their bulk equilibrium spacing. The rods tilt in the $x-y$ plane with an angle θ_b with respect to the x axis. So, for $g_{RC} \geq 0.5(\lambda/\nu)$, the rods are parallel to the x axis, while for $g_{RC} < 0.5(\lambda/\nu)$, they make an angle θ_b. The dimensionless free energy of the system, $F_{2,\perp} = F/(\gamma_{RC}\Omega_x\Omega_y)$, for the Sm A_2/Sm C_2 phase is then

$$F_{2,\perp} = 3H + 2\Gamma + \frac{2\lambda}{1+\lambda}\delta \qquad (9)$$

and we have used the relation $\cos\theta_b = (2\nu g_{RC}/\lambda)^{1/3}$ to obtain this equation. We only consider the bilayer phase because we discuss results in the strong segregation limit. Note that if the plates are the same, i.e., they have the same interfacial tensions with the polymer, the perpendicular state will always be favored over the antisymmetric state. The reason for this is the following. If the rods adjacent to the plates do not tilt, the perpendicular and anti-symmetric states have the same amount of rod−plate and coil−plate interfacial areas. However, the perpendicular state has less stretching energy compared with the antisymmetric state and so overall will always have less total free energy. This is the same as that with the conventional coil−coil system.[12] If the rods adjacent to the plates do tilt, then the perpendicular state will have less rod−plate surface area than the antisymmetric state and the above argument again follows.

4. Results and Discussion

4.1. Similar Plates. In the following results we have used the values $\lambda = 1$ and $\nu = 0.01$. These values for λ and ν result in a lamellar morphology in the bulk.[6,8,9] Let us first consider the effect of film thickness on the tilt angles θ and ψ. Figure 2 shows these tilt angles for $g_{RC} = 40$. This corresponds to an optimal bulk tilt angle of 0.38 rad. In this case the surface tension difference is $\delta = 0.15$ corresponding to the plates preferring rods over coils, and so Figure 2 plots tilt angles for the symmetric state. For $H < 1.1$ there is only one bilayer, and so only ψ is plotted here. The general feature of this graph is a periodiclike structure. Discontinuities occur at $H = n/\cos(0.38)$ where n is an integer. At this point the tilt angles are close to zero. Slightly above these values of H, the tilt angle jumps to a large value corresponding to an extra bilayer being added. The tilt angle then continuously decreases until another bilayer is added. Note that, in general, $\theta \neq \psi$ and also that, for H relatively small and near $n/\cos(0.38)$, ψ is zero. As explained above this minimizes the term $f_{surface}(i)$.

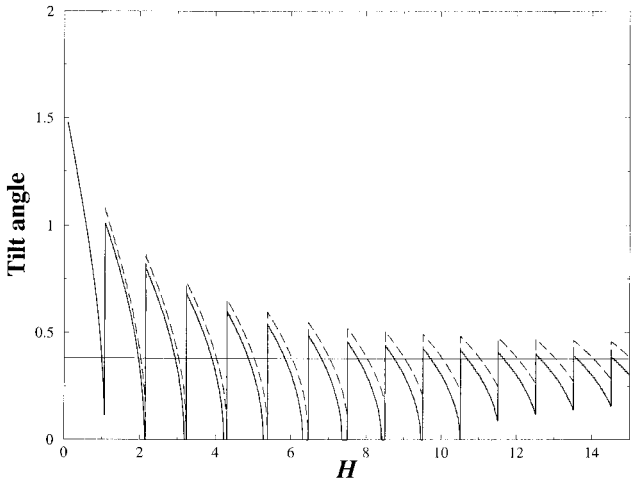

Figure 2. Tilt angles θ and ψ versus dimensionless plate separation H for $g_{RC} = 40$, $\Gamma = 0.1$, and $\delta = 0.15$. The full curve corresponds to ψ and the dashed curve to θ.

We consider now the case where $\delta > 0$, which implies the confining plates prefer rods to coils. Consider Figure 3a, which is a plot in the $H-\delta$ plane for $g_{RC} = 50$ showing where symmetric states only exist (unshaded) and where both symmetric and perpendicular states exist (shaded). For similar plates the free energy difference between symmetric, parallel, and perpendicular configurations is independent of Γ. Note that for $g_{RC} = 50$ the bulk state is a Sm A_2 phase, i.e., untilted bilayers. For sufficiently large δ, the symmetric state exists. This is to be expected because positive δ implies rods should be preferred at both plates. For smaller δ, we find that both symmetric and perpendicular states exist. Here even though the plates prefer rods, for a symmetric state when H is close to a half-integer, the stretching energy penalty paid by the coils is too large to overcome any rod−plate interfacial energy gain. As such, the perpendicular state is observed in this region. There is an important difference between the present rod−coil system and the conventional coil−coil system analyzed by Turner.[11] In Turner's system, lamellae can either expand or contract when H is not an integer; however, in our case for $g_{RC} \geq 50$, the lamellae may only contract and they cannot expand. The reason for this is simple: the maximum size of a Sm C_2/Sm A_2 lamellae is $2L(1 + \lambda)$. When the rods tilt, the lamellae must contract; i.e., their size is smaller at $2L(1 + \lambda)\cos\theta$, where θ is the tilt angle. Thus, as soon as the film thickness H is slightly larger than an integer, the perpendicular state has less free energy than the symmetric state. Thus, in our rod−coil system, for $g_{RC} = 50$, we observe a much larger region where the perpendicular state may be observed than in the corresponding coil−coil system.[11,12] In general, we can say our system is more constrained than Turner's system, and so the symmetric state is not as prevalent.

As the rod−coil surface tension, g_{RC}, decreases below 50, the system gets more freedom. When $g_{RC} < 50$ the bulk equilibrium state is a Sm C_2 state, i.e., tilted bilayers where the tilt angle is $\arccos[(2\nu g_{RC}/\lambda)^{1/3}] > 0$ and the lamellar size is $2L(1 + \lambda)(2\nu g_{RC}/\lambda)^{1/3} < 2L(1 + \lambda)$. In this case, because the bulk system has a nonzero tilt angle, there is additional freedom for the lamellar size; i.e., the lamellae can expand or contract about the bulk lamellar size. However, there is a limited freedom, because the maximum lamellar size is still $2L(1 + \lambda)$. On the other hand, as g_{RC} gets smaller, the system pays

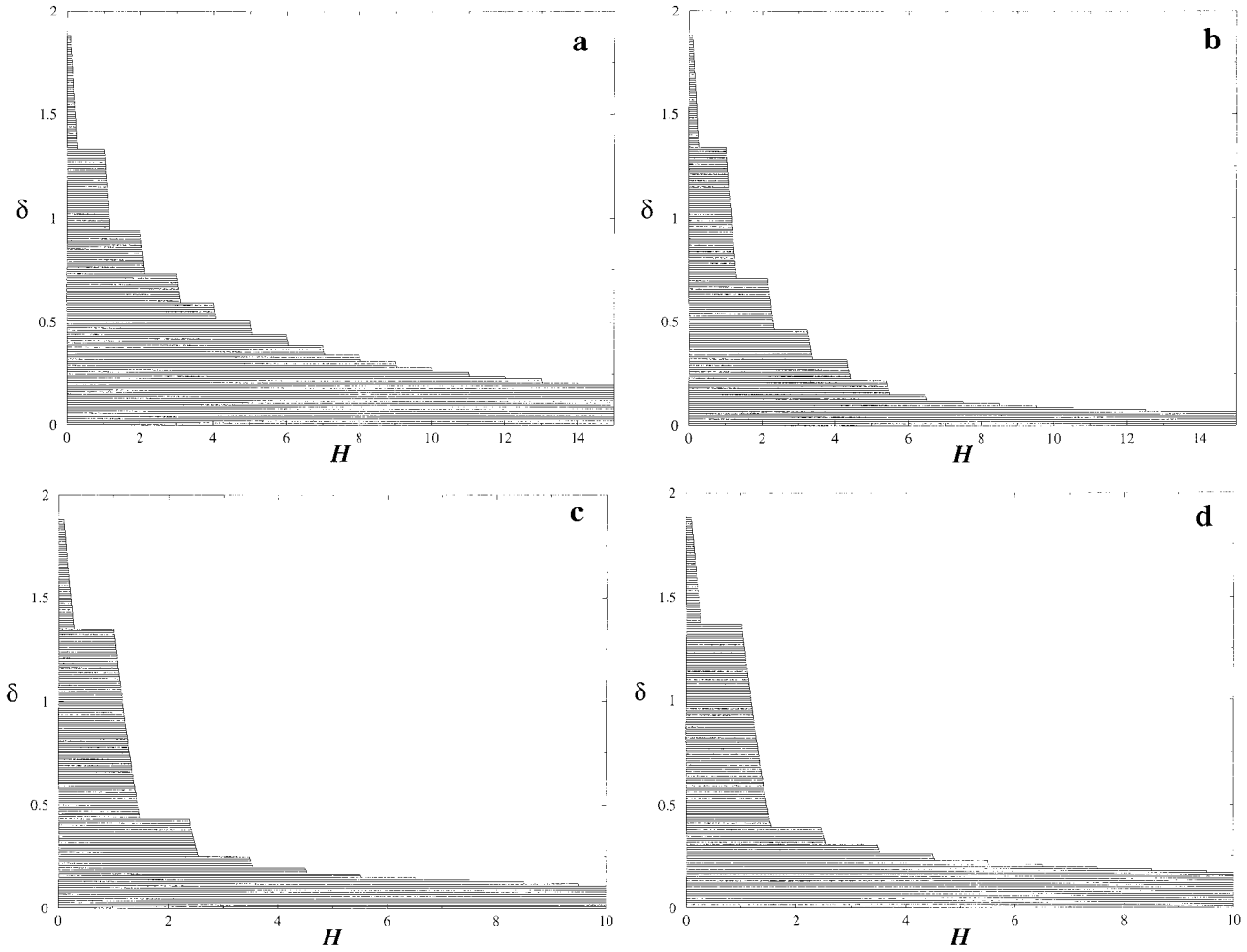

Figure 3. Plot in the $H-\delta$ plane (i.e., plate separation on the x axis and surface tension difference between the coil and the plates and the rod and the plates on the y axis) showing where symmetric states only exist (unshaded) and both symmetric and perpendicular states exist (shaded). The dimensionless rod−coil surface tensions (g_{RC}) are in each case (a) 50 (b) 40, (c) 20, and (d) 10.

a surface interfacial penalty for tilting; i.e., the $f_{surface}(i)$ term prevents ψ from having a large tilt. The above argument implies that as g_{RC} decreases, the perpendicular/symmetric region of the $H-\delta$ plane should initially decrease but then, as g_{RC} gets smaller, should plateau out before increasing again. Parts b−d of Figure 3, which are calculated for $g_{RC} = 40$, 20, and 10, respectively, show that as g_{RC} decreases, the shaded region initially decreases ($g_{RC} = 40$ and 20) before increasing again at small g_{RC} ($g_{RC} = 10$).

Consider Figure 4a, which is a plot of the dimensionless free energy (F/H) of the symmetric and perpendicular states versus H for $g_{RC} = 50$ and $\delta = 0.15$. The asymmetry of the symmetric state's free energy is quite evident; i.e., there are discontinuities in the free energy at $H = n$ ($n \in I$), corresponding to an extra bilayer being added. This is in contrast to the coil−coil system[11,12] where the symmetric states free energy is continuous. As a consequence, the perpendicular state exists for fairly thick films; i.e., even at $H \approx 10$ the perpendicular state has a lower free energy than the symmetric state. By $H \approx 20$ the symmetric state is able to distribute the strain over many layers, so that the perpendicular state no longer exists. For $g_{RC} = 40$ (Figure 4b), we now find that for $H > 7$ the symmetric state's free energy is continuous, while below this value it has jump discontinuities. For small thicknesses, $H/\cos\theta_b$ does not reach a half-integer and so there exists a discontinuity as another bilayer is added. For large thicknesses (i.e., $H > 7$) $H/\cos\theta_b$ is greater than a half-integer and so the free energy is continuous, although not smooth. Because the pressure is the derivative of the free energy, with respect to film thickness, these points would correspond to jumps in the pressure (discontinuities). As previously mentioned, we now observe the perpendicular state to exist only for $H < 6$, in contrast to the $g_{RC} = 50$ case. For $g_{RC} = 10$, we find the symmetric state is continuous for all H. Again, this is because the bulk tilt angle is large, roughly 0.95 rad, and so the lamellae have freedom to expand or contract. However, even though the lamellae have this freedom, we still observe the perpendicular state at $H = 10$. The reason for this is that a large tilt angle ψ makes the $f_{surface}(i)$ term large. This surface tension penalty results in an overall increase in the free energy of the symmetric state. Hence, the perpendicular state is observed up to $H = 10$.

In the case where the two similar confining plates prefer the coils, the surface energy $f_{surface}(i)$ becomes independent of g_{RC} (and therefore tilt angle). Thus, as g_{RC} increases, the region of the $H-\delta$ phase diagram occupied by both perpendicular and symmetric states will monotonically decrease (cf. Figure 3 where there is a minimum size of this region). The resulting free energy curves are quite similar to those in Figure 4 and so will not be shown.

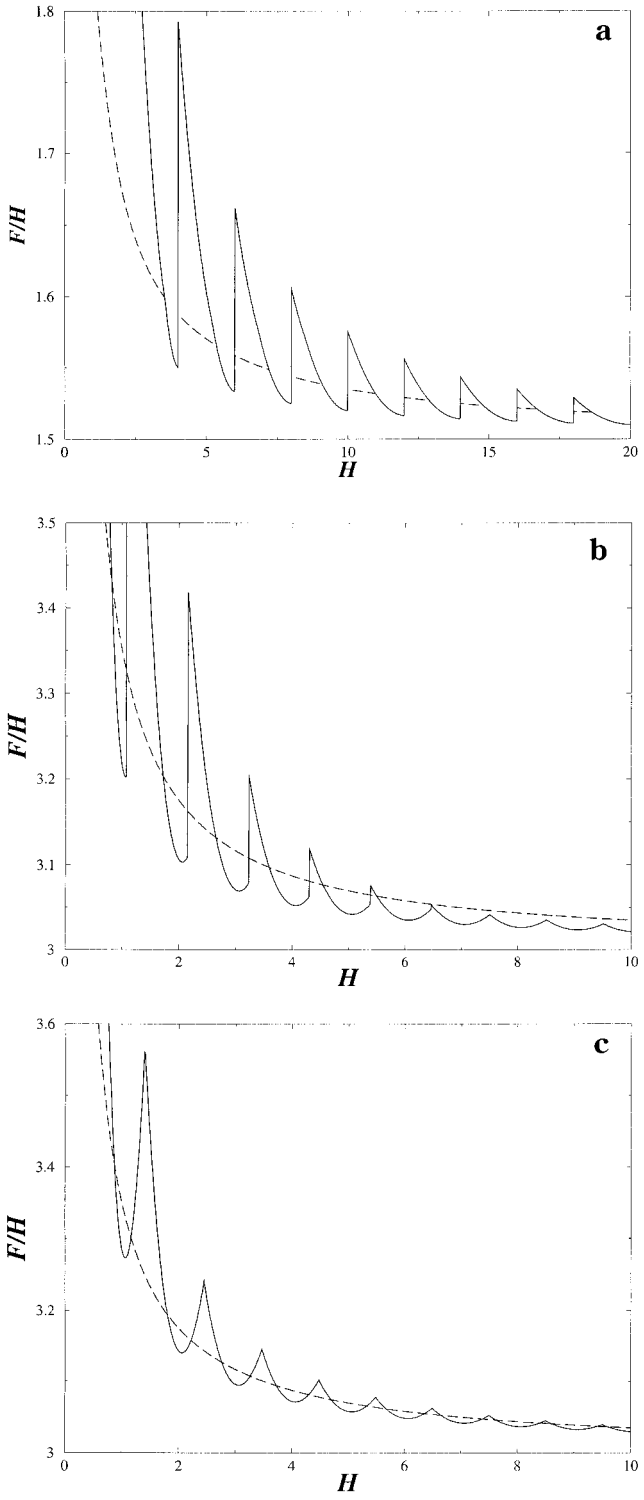

Figure 4. Free energy of the parallel symmetric (full curve) and perpendicular (dashed curve) states versus film thickness for a rod−plate/coil−plate surface tension difference of $\delta = 0.15$. Here the dimensionless rod−coil surface tension (g_{RC}) is varied in each case to be (a) 50 (b) 40, and (c) 10.

4.2. Dissimilar Plates. We may also consider the case where the confining plates are dissimilar. To do this, we need to define two sets of interfacial tensions, i.e., $\Gamma_1 \equiv \gamma_{RP1}/\gamma_{RC}$, $\delta_1 \equiv (\gamma_{CP1} - \gamma_{RP1})/\gamma_{RC}$ and $\Gamma_2 \equiv \gamma_{RP2}/\gamma_{RC}$, $\delta_2 \equiv (\gamma_{CP2} - \gamma_{RP2})/\gamma_{RC}$. We shall assume $\delta_1 > 0$, so that rods are preferred at plate 1, and $\delta_2 < 0$, so that the coils are preferred at plate 2. We also define two tilt angles, ψ_1 and ψ_2, for the case where rods are at both plates. We can use eqs 6 and 8, modified in an obvious fashion, to determine the free energies of the various possible states. The surface energies are given by

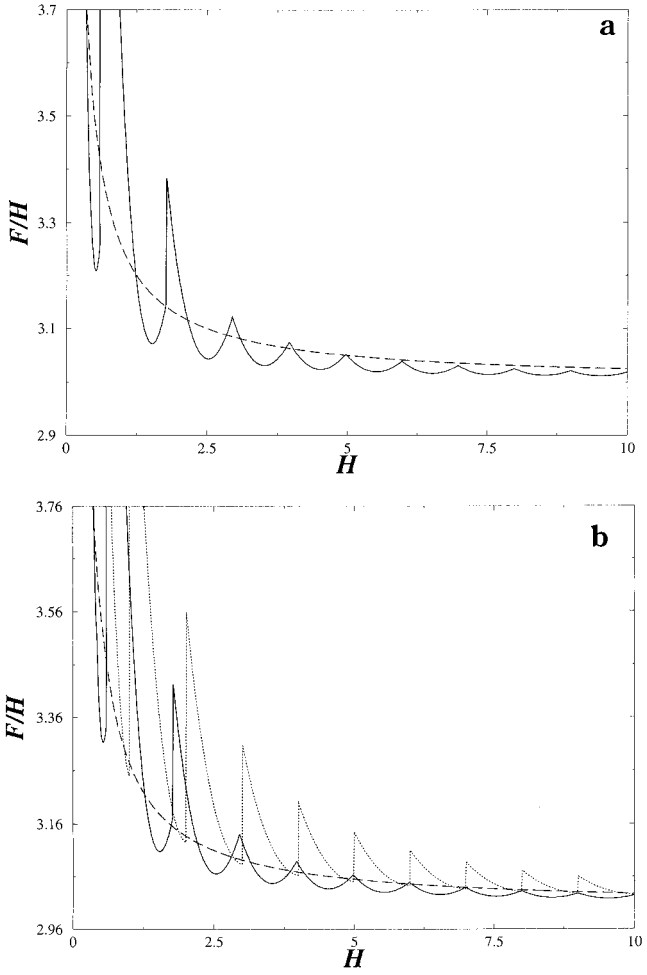

Figure 5. (a) Free energy of the parallel antisymmetric (full curve) and perpendicular (dashed curve) states versus film thickness for a rod−coil surface tension $g_{RC} = 30$. The other parameters are $\delta_1 = 0.05$, $\Gamma_1 = 0.15$, $\delta_2 = -0.15$, and $\Gamma_2 = 0.2$. (b) Free energy of the parallel antisymmetric (full curve), parallel symmetric (dotted curve), and perpendicular (dashed curve) states versus film thickness for $g_{RC} = 30$, $\delta_1 = 0.1$, $\Gamma_1 = 0.1$, $\delta_2 = -0.15$, and $\Gamma_2 = 0.2$.

$$
\begin{aligned}
i = 1 \qquad & f_{\text{surface}}(i) = \Gamma_1 (2 - \cos \psi_1) + \Gamma_2 (2 - \cos \psi_2) \\
i = 2 \qquad & f_{\text{surface}}(i) = \Gamma_1 (2 - \cos \psi_1) + \Gamma_2 + \delta_2 \\
i = 3 \qquad & f_{\text{surface}}(i) = (\Gamma_1 + \delta_1) + (\Gamma_2 + \delta_2) \qquad (10)
\end{aligned}
$$

If there are rods at both plates, then we must minimize the resulting free energy over three angles, while in the other cases minimization is done over fewer angles. Once again the minimization scheme is carried out numerically.

We must also consider the free energy of the perpendicular lamellar morphology, which has a derivation similar to that of eq 9. Doing this, one finds that for the case of dissimilar plates the dimensionless free energy of this state is

$$F_{2,\perp} = 3H + \Gamma_1 + \Gamma_2 + \frac{\lambda}{1+\lambda}(\delta_1 + \delta_2) \qquad (11)$$

In Figure 5a the free energy curves for $g_{RC} = 30$ are shown, for $\Gamma_1 = 0.05$, $\delta_1 = 0.15$, $\Gamma_2 = 0.2$ and $\delta_2 = -0.15$.

This corresponds to antisymmetric plates; i.e., plate 1 prefers rods as much as plates 2 prefers coils. In this case the two competing free energy states are the antisymmetric parallel configuration and the perpendicular configuration. The forms of the free energy curves are similar to those of Figure 4, with transitions from perpendicular to parallel configurations as H increases. Figure 5b shows the scenario for $g_{RC} = 30$, $\Gamma_1 = 0.1$, $\delta_1 = 0.1$, $\Gamma_2 = 0.2$, and $\delta_2 = -0.15$, so that coils have greater preference at plate 2 than rods have at plate 1; i.e., $\gamma_{CP2}/\gamma_{RC} = 0.05$ and $\gamma_{RP1}/\gamma_{RC} = 0.1$. Thus, we now have three competing states—parallel antisymmetric perpendicular, and parallel symmetric with coils at both plates. For H relatively small and close to an integer value, the parallel symmetric state is the lowest free energy state. Thus, even though there is a surface energy penalty for having coils at plate 1, because the lamellae are close to their bulk spacing, the parallel symmetric state is favored.

5. Conclusions

In this paper we have studied the equilibrium morphology of a confined symmetric rod−coil diblock melt thin film. In the case of similar plates we find either parallel lamellae in a symmetric configuration or perpendicular lamellae. For dissimilar plates three states can exist. These are the two already mentioned plus a parallel, antisymmetric morphology. In contrast to coil−coil melts,[11,12] we find our system is much more constrained because there is an absolute maximum size of a lamellae, $2L(1 + \lambda)$, and also the plate−rod interfacial terms penalize large tilts of the rods adjacent to the plates. As a result, the perpendicular state is observed for relatively large thicknesses. In addition in the present system, because rods adjacent to the plates tilt at an angle different from that of rods in the interior, lamellae adjacent to the plates have a different width from that of lamellae in the interior.

Our study is not exhaustive, in that we have limited ourselves to a few numerical examples. However, we believe the general trends we have found will be valid for a wide range of parameters.

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