Macromolecules **1999,** *32,* 8115−8120

Diblock Copolymer Melts in Electric Fields: The Transition from Parallel to Perpendicular Alignment Using a Capacitor Analogy

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Received May 25, 1999

ABSTRACT: We consider alignment of a symmetric diblock copolymer melt thin film or bulk phase by an electric field using a capacitor analogy. For the lamellar phase we show that alignment of the lamellae in the direction perpendicular to the bounding electrodes, compared to parallel alignment, occurs for thicker films. For thin films the critical electric field required for a transition from parallel to perpendicular alignment is proportional to $H^{-1/2}$, where H is the film thickness. We also consider the possibility of a mixed lamellar morphology where, because the bounding electrodes prefer one block, parallel layers form adjacent to the electrodes, while in the interior region there is perpendicular alignment. We determine the conditions for such a morphology.

1. Introduction

Diblock copolymers consist of two homopolymers joined together at one end. A melt of such polymers can self-assemble into various microphases such as lamellae, cylinders, or spheres.[1] The microphase separation is driven by the enthalpic incompatibility of the two blocks and is opposed by the stretching entropy of the chains. In this paper we will concentrate on symmetric diblocks where a lamellar phase is formed. In principle the equilibrium state of such a diblock melt consists of well-ordered lamellae which also are well-aligned with each other. In practice a system quenched into the melt state often consists of poorly aligned lamellae or domains of lamella which are aligned in different directions. This situation is not satisfactory for many practical situations and also for many experiments. Because the thermodynamic driving force for alignment is weak, and the kinetics slow, external fields have been used to drive alignment. Mechanical shearing proved to be successful in this regard.[2] Our interest here is in alignment by an electric field, which has been carried out successfully in a series of experiments.[3−6] The most recent experiments by Morkved et al.[5] and Mansky et al.[6] were conducted on polystyrene-poly(methylmethacrylate) (PS-PMMA) diblock copolymers with a PS volume fraction of 0.66. Thus, a bulk phase of this melt has a cylindrical morphology. The silicon nitride electrodes imposed an electric field on the sample and the dielectric permittivities of these materials (compared to the permittivity of a vacuum) were $\epsilon_{PS} = 2.45$ and $\epsilon_{PMMA} \approx 6$. Strong alignment of the cylinders parallel to the electric field lines was observed for fields in excess of 30 kV/cm.

In this paper we begin by explaining, in simple terms, why an electric field aligns microphases in the strong segregation limit. The strong segregation limit corresponds to $\chi N \gg 50$, where χ is the Flory−Huggins interaction parameter (between blocks) and N is the number of monomers in each block. We study in detail the case of a diblock melt confined between two plates (bounding electrodes). Our study should be seen in part as being complementary to the earlier studies which examined alignment in the limit of weaker segregation.[3,4]

Consider a symmetric diblock copolymer melt which in the strong-segregation limit forms a lamellar phase. The diblocks are made up of A and B blocks, with each block consisting of N monomers of size a. We denote the thickness of one bilayer (i.e., AB-BA) of this phase in the bulk by L_2 which is given by[1,7,8] $L_2 = 4[(6\gamma_{AB}a^5)/(\pi^2 k_B T)]^{1/3} N^{2/3}$, where γ_{AB} is the AB interfacial tension and T is the temperature. Note that γ_{AB} and χ are related by $(\gamma_{AB}a^2)/(k_B T) = (2\chi/3)^{-1/2}$. We now place the sample between two identical flat parallel plates each of area A separated by a distance H. The area of the plates is assumed to be large $A \gg H^2$ so we do not have to deal with edge effects, both for the electric field and the interfacial energy. There are two simple orientations for the lamellar phase between the plates (Figures 1 and 2). These are the parallel orientation, Figure 1(a) and the perpendicular orientation, Figure 2(a). In general there will be a preference for one of the blocks to lie at the surface of the plates, this preference being governed by the polymer−plate interfacial tensions γ_{AP} and γ_{BP}. This will tend to favor the parallel arrangement of the lamellae. However, by applying a voltage across the plates it is possible to induce perpendicular alignment. This can be explained as follows. In each case the system acts as an electric capacitor with capacitance $C_{\|}$ or $C_{\perp}$. Under conditions of constant applied voltage, V, the energy stored in a capacitor of capacitance C is $^1/_2CV^2$ and hence the free energy of the system is[9−12] $-\,^1/_2CV^2$. Note that the free energy is negative, i.e., a capacitor connected to a battery will charge spontaneously. Under conditions of fixed potential difference V between the plates the system prefers to maximize its capacitance. In the parallel configuration the system can be viewed as a sequence of capacitors (each one made of either pure block A or pure block B) in series, Figure 1(b). In the perpendicular configuration the system can be viewed as a sequence of capacitors acting in parallel, Figure 2(b). We will show below that this difference implies $C_{\|} < C_{\perp}$ and hence the perpendicular configu-

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10.1021/ma9908200 CCC: $18.00

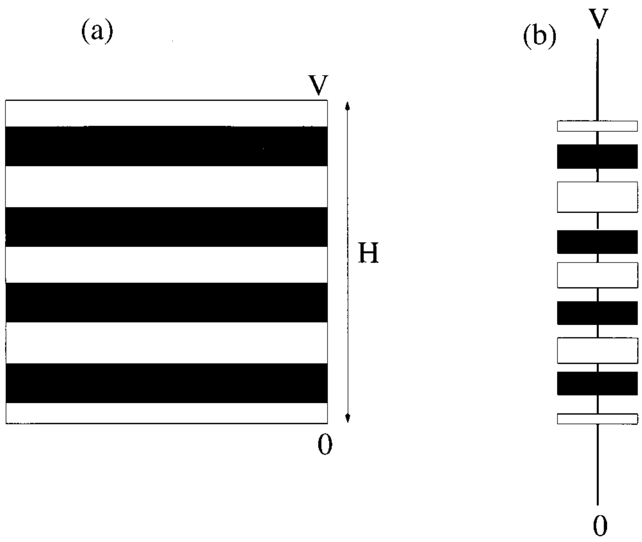

Figure 1. (a) Side view of a schematic of the diblock copolymer melt where the lamellae are oriented parallel to the bounding plates. A blocks are white and B blocks are black. (b) A schematic of the equivalent electrical circuit where the capacitors are in series.

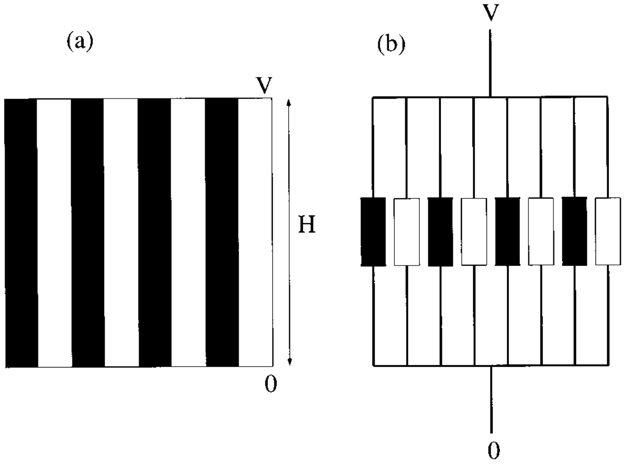

Figure 2. (a) Side view of a schematic of the diblock copolymer melt where the lamellae are oriented perpendicularly to the bounding plates. A blocks are white and B blocks are black. (b) A schematic of the equivalent electrical circuit where the capacitors are in parallel.

ration is favored by an applied voltage. On a more qualitative level alignment occurs because the electric field lines connecting each plate prefer to travel by easy paths, through whichever block has the highest polarizability. In the perpendicular orientation this is readily done. In the parallel orientation the electric field lines are forced to traverse both blocks evenly and hence this configuration is not favored.

2. The Case of an Unstrained Layer: A Thick Film

We now present the calculation in detail. We first consider the parallel orientation (Figure 1). We assume for simplicity that the distance H between the plates is chosen so that an integral number of equilibrium bilayers is always accommodated, i.e., $H = mL_2$ where m is an integer. This implies that the layer is unstrained. For m bilayers the total number of interfaces between blocks A and B is $n_{AB} = 2m$. We will assume that block A prefers the plates, i.e., $\gamma_{AP} < \gamma_{BP}$. The total number of A-plate interfaces is 2 so that the total interfacial energy for plates of area A is

$$F_I = 2A(m\gamma_{AB} + \gamma_{AP}) \tag{1}$$

We will call the total stretching energy per monolayer per unit area S. The total stretching energy is then $F_S = 2AmS$ and hence, the total polymeric free energy is

$$F_{\mathrm{polymer}\|} = 2A(m\gamma_{AB} + \gamma_{AP} + mS) \tag{2}$$

For the electrical part of the free energy we require the total capacitance of the system which consists of three parts: (i) m capacitors with material B as a dielectric, each of thickness $w = L_2/2$; (ii) $m - 1$ capacitors with material A as dielectric, each of thickness w; and (iii) Two capacitors (nearest each plate) made of block A but with thickness $w/2$. All of these capacitors are in series. The total capacitance is then[9-12] $C_{\|} = (mC_B^{-1} + (m-1)C_A^{-1} + 2\,C_*^{-1})^{-1}$, where $C_i = \epsilon_i A/w$, $C_* = 2\epsilon_A A/w$, and ϵ_i is the dielectric constant for the material making up block i. Hence, the total capacitance is $C_{\|} = A\epsilon_{\|}/(mw)$, where $\epsilon_{\|} = (\epsilon_A^{-1} + \epsilon_B^{-1})^{-1}$. The total free energy per unit area in the parallel configuration is then

$$F_{\|} = 2\gamma_{AP} + 2m(\gamma_{AB} + S) - \frac{V^2}{H}\epsilon_{\|} \tag{3}$$

In the perpendicular orientation (Figure 2) the total plate–polymer energy is $A(\gamma_{AP} + \gamma_{BP})$. The total surface energy between the blocks and the total stretching energy is identical to the parallel orientation. Hence, the total polymer contribution to the free energy, per unit area of the plates, in the perpendicular orientation is

$$F_{\mathrm{polymer}\perp} = (\gamma_{AP} + \gamma_{BP} + 2m\gamma_{AB} + 2mS) \tag{4}$$

In the perpendicular orientation we have m capacitors of material A and m capacitors of material B in parallel. The height of each capacitor is H and the area of each capacitor is $A/(2m)$. The total capacitance is then $C_\perp = mC_A + mC_B$, where $C_i = A/(2mH)\epsilon_i$. The total capacitance of the entire system is then $C_\perp = 2A\epsilon_\perp/H$, where $\epsilon_\perp = (\epsilon_A + \epsilon_B)/4$. The total free energy per unit area in the perpendicular orientation is

$$F_\perp = \gamma_{AP} + \gamma_{BP} + 2m\gamma_{AB} + 2mS - \frac{V^2}{H}\epsilon_\perp \tag{5}$$

Comparing just the electrical parts of the free energies, we have $F_{E\|} - F_{E\perp} = V^2 H^{-1}(\epsilon_\perp - \epsilon_{\|})$ and $\epsilon_\perp - \epsilon_{\|} = (\epsilon_A - \epsilon_B)^2/[4(\epsilon_A + \epsilon_B)] > 0$. It is clear from this that the electrical part of the free energy is larger in the parallel orientation except in the case when the two blocks have the same dielectric constant. However, it is also clear that the perpendicular orientation has a higher free surface free energy due to the unfavorable interface between block B and the plate. The difference in the total free energy between the two orientations is $\Delta F \equiv F_\perp - F_{\|}$, and is given by

$$\Delta F = (\gamma_{BP} - \gamma_{AP}) - \frac{V^2}{H}(\epsilon_\perp - \epsilon_{\|}) \tag{6}$$

Equating the free energies in the perpendicular and parallel orientations gives the critical potential difference, V_c that needs to be applied to convert between the two. This is

$$V_c = [(\gamma_{BP} - \gamma_{AP})\,(\epsilon_\perp - \epsilon_{\|})^{-1}\,H]^{1/2} \tag{7}$$

This suggests for a given plate separation, that a small voltage favors a parallel orientation of the lamellae, whereas a large voltage favors a perpendicular orientation of the lamellae. Thus, on increasing the voltage a parallel-to-perpendicular transition results. Another way of viewing the experiments is to ask what is the critical electric field required to induce a parallel-to-perpendicular transition. Defining $E_{\perp,\|} \equiv V_c/H$, we find

$$E_{\perp,\|} = \left[\frac{\gamma_{BP} - \gamma_{AP}}{\epsilon_\perp - \epsilon_{\|}}\right]^{1/2} H^{-1/2} \tag{8}$$

For a given plate separation, for $E < E_{\perp,\|}$, a parallel orientation results, whereas for $E > E_{\perp,\|}$, a perpendicular orientation is induced. Note that for very thin films the average electric field can be very great indeed and can exceed the breakdown field of the material. We will give numerical estimates of this field for realistic experimental scenarios in the next section.

3. Strained Thin Films

In the previous section we considered the case where an integral number of lamellae with the bulk spacing were able to fit between the plates. However, in many experimental situations thin films of diblock will be used and in these cases there can be large strains induced in the system. These strains occur because the bulk bilayer spacing is not commensurate with the film thickness. These intrinsic strains can, for instance, induce a change from the parallel to the perpendicular alignment, even in the absence of electric fields.[13] Here we examine how these strains affect the above calculation.

Initially consider a parallel orientation of the lamellae between the two plates. If the distance H between the two plates is not an integral multiple of the bulk equilibrium bilayer spacing L_2, the system may either have $n_l = m$ (m an integer) bilayers or $n_l = m \pm {}^1/_2$ bilayers between the plates. Here m is the closest integer[14] to H/L_2. The first case is the so-called symmetric case, whereas the second is antisymmetric. The ± sign is used here to denote the fact that an antisymmetric configuration, i.e., AB...AB, may have one monolayer less or one monolayer more than a symmetric configuration. The free energy of a polymer chain is a sum of AB interfacial energy and chain entropy or stretching. Assuming Gaussian statistics for the bond lengths, one can show that the chain entropy is proportional to $k_BL^2/(Na^2)$, where L is the distance through which each chain is stretched. Hence, the free energy due to the polymer itself is

$$F_{\text{polymer},\|} = Q\left[\frac{\pi^2 k_B T}{48Na^2}(2H/n_l)^2 + \gamma_{AB}\frac{2Na^3}{(2H/n_l)}\right] \tag{9}$$

where Q is the total number of diblock chains in the sample. This can be determined by a simple volume conservation relation to be $Q = AH/(2Na^3)$. Using this expression for Q and the expression for L_2, the polymer energy becomes

$$F_{\text{polymer},\|} = 2A\gamma_{AB}\left[\frac{H^3}{2L_2^3\,n_l^2} + n_l\right] \tag{10}$$

The surface energy will be $2\gamma_{AP}A$ if the diblocks are in a symmetric configuration or $(\gamma_{AP} + \gamma_{BP})A$ for an antisymmetric configuration. To determine the electrical part of the free energy, in the parallel orientation, we note that the layers at each plate have half the thickness of the other layers. Thus, if we have n_l bilayers between the plates, the thickness of the A or B materials adjacent to the plates is $H/(4n_l)$, whereas other layers have thickness $H/(2n_l)$. Thus, the capacitance of the surface layers is $C_i^{\text{surf}} = 4A\epsilon_i n_l/H$, whereas the capacitance of the middle layers is $C_i^{\text{middle}} = 2A\epsilon_i n_l/H$. Evaluating the total capacitance of the system, one finds in either case we get $C_i = [(2A)/H]\epsilon_{\|}$. The total free energy per unit area in the parallel configuration, for an antisymmetric configuration, is

$$F_{\|}^{as} = \gamma_{AB}\left[\frac{H^3}{L_2^3\,n_l^2} + 2n_l\right] + \gamma_{AP} + \gamma_{BP} - E_{av}^2 H\epsilon_{\|} \tag{11}$$

where $n_l = m \pm {}^1/_2$. For a symmetric configuration this quantity is

$$F_{\|}^{s} = \gamma_{AB}\left[\frac{H^3}{L_2^3\,n_l^2} + 2n_l\right] + 2\gamma_{AP} - E_{av}^2 H\epsilon_{\|} \tag{12}$$

where $n_l = m$.

In the perpendicular orientation, the calculation is easier because each block has the same spacing, $L_2/2$. So the contribution to the free energy from polymer and surface parts is

$$F_{\text{polymer},\perp} = A\left[\gamma_{AB}\frac{3H}{L_2} + \gamma_{AP} + \gamma_{BP}\right] \tag{13}$$

The electric field contribution is the same as that calculated in Section 2, so that the total free energy in the perpendicular orientation, per unit area of the plates is

$$F_\perp = \left[\frac{3\gamma_{AB}H}{L_2} + \gamma_{AP} + \gamma_{BP}\right] - E_{av}^2 H\epsilon_\perp \tag{14}$$

The plate−diblock interfacial tensions favor a parallel orientation because one block normally wets the substrate in preference to the other, i.e., for a PS-PMMA diblock melt on a silicon substrate the PMMA block preferentially wets the substrate.[15] However, the stretching energy favors a perpendicular orientation, because in this case the diblocks always obtain their equilibrium bulk spacing. As in the case of thick films, the electric field also favors a perpendicular orientation.

Let us consider now the effect of the electric field on alignment of the lamellae. Figure 3 is calculated for a set of parameters obtained from the experimental works of Morkved et al.,[5] Kellog et al.,[15] and Mansky et al.[16] Note that we use an electric field an order of magnitude larger than Morkved et al., to obtain a transition at relatively small H. Experiments by Morkved et al. were for the cylindrical phase of diblocks, and for very large electrode separations. They did not specifically address the issue of the transition from a nonaligned to aligned sample. Also, although the parameters are the same as those used by Morkved et al.,[5] our calculations are for

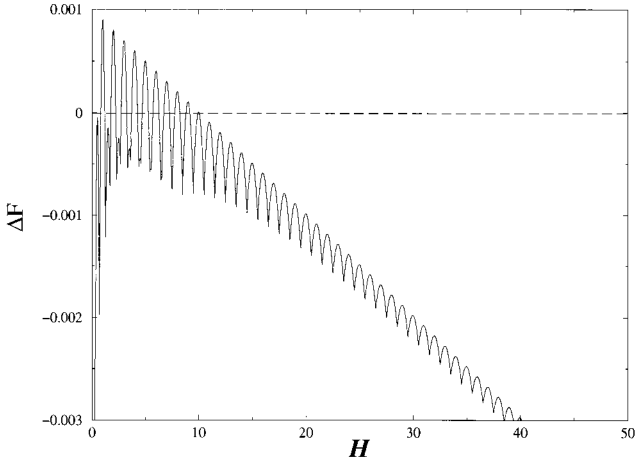

Figure 3. Free energy difference $\Delta F \equiv F_\perp - F_\parallel$ versus H (scaled thickness) for $\gamma_{BP} - \gamma_{AP} = 0.001$ J/m^2 , $E = 3.7 \times 10^7$ N/C, $\epsilon_A = 2.17 \times 10^{-11}$ C^2 N^{-1} m^{-2}, $\epsilon_B = 5.31 \times 10^{-11}$ C^2 N^{-1} m^{-2}, $\gamma_{AB} = 0.01$ J/m^2, and $L_2 = 2.2 \times 10^{-8}$ m. Dashed line is $\Delta F = 0$, for $\Delta F > 0$ the parallel state is favored, whereas for $\Delta F < 0$ the perpendicular state is favored.

a slightly different geometry which we briefly discuss in the conclusion. In Figure 3 we plot $\Delta F = F_\perp - F_\parallel$ versus H so that when $\Delta F > 0$ the parallel phase is favored, whereas when $\Delta F < 0$ the perpendicular phase is favored. The shape of the free energy curve has a characteristic "discrete" lamellar form,[14] in that there exist finite intervals in which the function is smooth. For ultrathin films a perpendicular orientation is preferred. Note that perpendicular alignment occurs even in the absence of an electric field.[13] However, the electric field additionally favors a perpendicular alignment. As the thickness of the film increases, the diblocks are able to relieve their strain more easily in parallel alignment. As such, the system transfers to parallel alignment. This parallel alignment is most favored when $H \equiv H/L_2$ is an integer, i.e., the diblocks achieve their bulk, equilibrium spacing. As the film thickness increases further, at constant field, the effect of the electric field becomes more pronounced. At approximately $H_c = 8$ the system reverts to perpendicular alignment. The free energy contribution due to the electric field is roughly proportional to film thickness, so that at large thicknesses one should achieve perpendicular alignment. From Section 2, we can also get an estimate for the critical thickness at which the system transfers from parallel to perpendicular alignment. Using the parameters given in Figure 3 and eq 8, we find $H_c \approx 11$. This compares quite well with the result we have obtained from the detailed calculation.

4. Mixed Parallel−Perpendicular Phases

In the above discussions, we have assumed that the system was always in either the parallel or perpendicular orientation. The parallel orientation is favored by the block−plate interfacial tensions, whereas the perpendicular orientation is favored by the electric field. In practice it might be more favorable to have a mixed phase, with a parallel monolayer near each of the plates and the remainder of the system perpendicular, as shown in Figure 4. The parallel monolayers allow the plates to be coated with favorable polymer while the perpendicular central region lowers the electrical energy. The price paid for this configuration is an increased polymer−polymer surface energy where the parallel and perpendicular regions meet. In principle the mixed phase has a smoother crossover between parallel and perpendicular geometries[17] and our estimate of the free energy is thus only an upper bound.

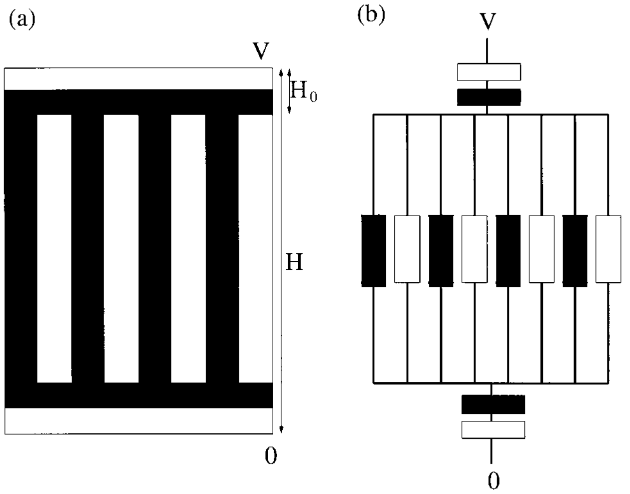

Figure 4. (a) Side view of a schematic of the diblock copolymer melt where the lamellae are in a mixed lamellar configuration. In the region the lamellae are oriented parallel to the bounding plates, with A blocks being preferred by the plates, whereas in the interior region there is perpendicular alignment of the lamellae. A blocks are white and B blocks are black. (b) A schematic of the equivalent electrical circuit.

In this case we assume that a parallel lamellae region of thickness H_0 exists adjacent to each plate (see Figure 4). In practice this may be only a monolayer thick, i.e., $L_2/2$ units. At this stage we shall not assume this, and rather minimize over all possible H_0, where $0 < H_0 < H/2$. The polymeric part of the free energy is just a combination of twice the parallel alignment, for thickness H_0, and a perpendicular alignment for thickness $H - 2H_0$, plus an extra AB interfacial term due to the additional AB interface at the junction between perpendicular and parallel orientations. For the electrical part of the free energy we note that the system consists of three sets of capacitors in series. These are (i) parallel alignment contribution of capacitance $C_\parallel = [(2A/(H_0)]\epsilon_\parallel$, (ii) perpendicular alignment contribution of capacitance $C_\perp = [(2A)/(H - 2H_0)]\epsilon_\perp$, and (iii) another parallel alignment contribution as given in (i). The total capacitance of the system is then $C_m = [2C_\parallel^{-1} + C_\perp^{-1}]^{-1}$. Thus, for a mixed configuration we obtain the free energy of the system as

$$F_m = \gamma_{AB}\left[\frac{2H_0^3}{L_2^3\, n_1^2} + 4n_1 + \frac{3(H - 2H_0)}{L_2} + 1\right] + 2\gamma_{AP} - \frac{1}{2}E_{av}^2 H^2\left[\frac{H_0}{\epsilon_\parallel} + \frac{1}{2\epsilon_\perp}(H - 2H_0)\right]^{-1} \quad (15)$$

Here $n_1 = m$, i.e., the closest integer to $2H_0/L_2$, for a symmetric mixed configuration, and for an antisymmetric mixed configuration, $n_1 = m \pm {}^1/_2$.

Let us initially consider the case where there is only one monolayer of parallel lamellae near each plate. If we now compare this free energy with the free energy of the parallel and perpendicular states in the continuum limit we find the critical field for a perpendicular-to-mixed-state transition is $E_{\perp m}$ and is given by

$$E_{\perp \mathrm{m}} = \left[\frac{((\gamma_{\mathrm{BP}} - \gamma_{\mathrm{AP}}) - \gamma_{\mathrm{AB}})(\epsilon_{\perp} + \epsilon_{\parallel}(H-1))}{L_2\epsilon_{\perp}(\epsilon_{\perp} - \epsilon_{\parallel})H}\right]^{1/2} \tag{16}$$

Thus when $\gamma_{\mathrm{BP}} - \gamma_{\mathrm{AP}} > \gamma_{\mathrm{AB}}$, the mixed state will be favored over purely perpendicular alignment. The critical field for a parallel to mixed state transiton is $E_{\parallel \mathrm{m}}$ and is given by

$$E_{\parallel \mathrm{m}} = \left[\frac{\gamma_{\mathrm{AB}}(\epsilon_{\perp} + \epsilon_{\parallel}(H-1))}{L_2\epsilon_{\parallel}(\epsilon_{\perp} - \epsilon_{\parallel})H(H-1)}\right]^{1/2} \tag{17}$$

The mixed state exists because of the affinity of the plates for the A blocks. This is at the expense of extra AB interfacial area at the junction between parallel and perpendicular alignment. In Figure 5 we plot the difference $\Delta G \equiv F_{\mathrm{m}} - F_{\parallel}$ versus H. Note that as far as the mixed and parallel configurations are concerned there is no effect of diblock−plate surface tension because both configurations have A blocks adjacent to the plates for $(\gamma_{\mathrm{BP}} - \gamma_{\mathrm{AP}})/\gamma_{\mathrm{AB}} > 1.0$. For these parameters we find the transition to a mixed configuration occurs for fairly thick films, i.e., approximately $H_{\mathrm{c}} = 100$. As in Figure 3, we see that the free energy difference is roughly proportional to H, so that for large thicknesses, at constant electric field, the mixed state is favored. From eq 17 we find the critical number of layers for this transition is $H_{\mathrm{c}} \approx 111$ which, again, is quite close to the more detailed calculations.

Finally, we consider the phase diagram for this system. The transitions among parallel, perpendicular, and mixed alignment states are given approximately by eqs 8, 16, and 17. In principle there are three variables: E, H, and $(\gamma_{\mathrm{BP}} - \gamma_{\mathrm{AP}})/\gamma_{\mathrm{AB}}$. If $(\gamma_{\mathrm{BP}} - \gamma_{\mathrm{AP}}) < \gamma_{\mathrm{AB}}$, the perpendicular state is favored over the mixed state. In this case Figure 6(a) gives a typical slice, in the $E - H$ plane, of the phase diagram. For ultrathin films, i.e., less than a monolayer, perpendicular alignment is favored because this is the only way the lamellae can be close to their preferred spacing.[13] As the film gets thicker, parallel alignment is observed. The critical curve defining the transition from perpendicular to parallel alignment is given by eq 8. For $(\gamma_{\mathrm{BP}} - \gamma_{\mathrm{AP}}) > \gamma_{\mathrm{AB}}$ the mixed state is favored over the perpendicular state. In this case we simplify the expression for the parallel−mixed state transition, eq 17, by assuming that H is large. Thus, eq 17 becomes $E_{\parallel \mathrm{m}} \approx \gamma_{\mathrm{AB}}^{1/2}[(\epsilon_{\perp} - \epsilon_{\parallel})L_2 H]^{-1/2}$. Figure 6(b) gives a typical slice of the phase diagram for $(\gamma_{\mathrm{BP}} - \gamma_{\mathrm{AP}}) > \gamma_{\mathrm{AB}}$.

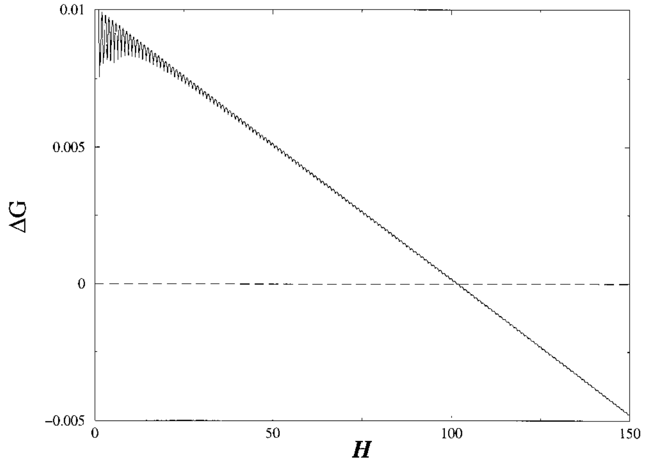

Figure 5. Free energy difference $\Delta G \equiv F_{\mathrm{m}} - F_{\parallel}$ versus H for the same parameters as in Figure 3 except $\gamma_{\mathrm{BP}} - \gamma_{\mathrm{AP}} = 0.015$ J/m^2. Dashed line is $\Delta G = 0$, for $\Delta G > 0$ the parallel state is favored, whereas for $\Delta G < 0$ the mixed state is favored.

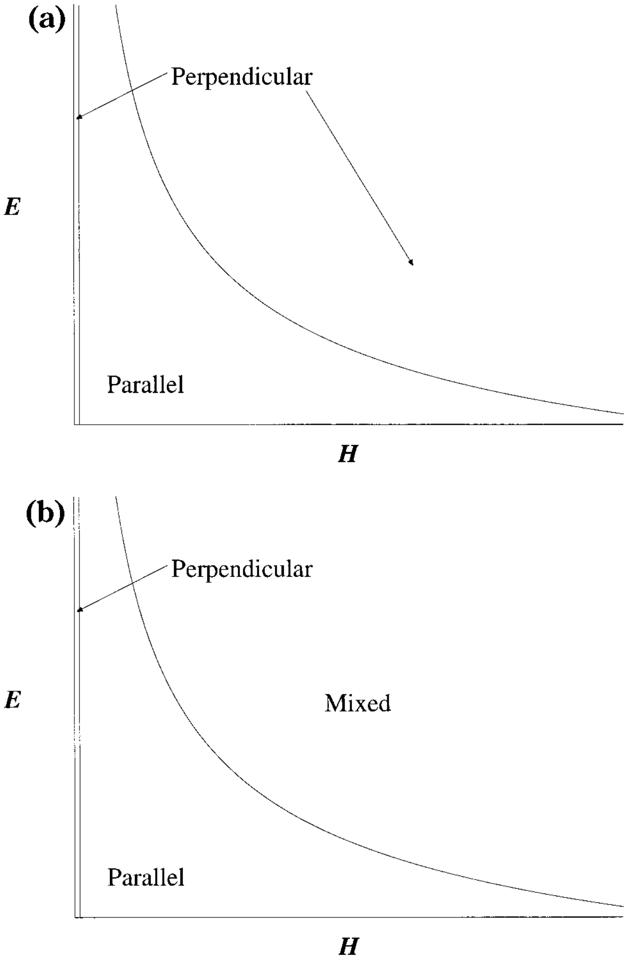

Figure 6. Phase diagram for system for a typical slice in the $E - H$ plane such that (a) $\gamma_{\mathrm{BP}} - \gamma_{\mathrm{AP}} < \gamma_{\mathrm{AB}}$ (b) $\gamma_{\mathrm{BP}} - \gamma_{\mathrm{AP}} > \gamma_{\mathrm{AB}}$.

5. Conclusion

In this paper we have given a simple explanation for the alignment of diblock melts by electric fields in the strong segregation limit. We studied the case of a melt placed between two plates, which usually favors alignment parallel to the plates. The electric field enhances alignment of the lamellar interfaces parallel to the electric field lines, i.e., perpendicular to the plates. In general this occurs for thicker films, the critical field being roughly proportional to $H^{-1/2}$. We predict that a mixed state will form when the preference of the plates for one block is sufficiently large and the film is sufficiently thick. This mixed state consists of a parallel monolayer at the plates followed by perpendicular alignment in the remainder of the system. We have concentrated here on the lamellar phase of a diblock melt. However, our capacitance analogy is also applicable to other morphologies, in particular the cylindrical geometry.[18] This was treated in recent experimental studies by Morkved et al.,[5] Mansky et al.,[6] and Russell's group,[19] who have shown that electric fields may also be used to align these systems. The geometries in these experiments were slightly different than our geometry. In the experimental case the electrodes are in the plane of the thin film sample, i.e., in the direction parallel to the film thickness. Our model is not quantitatively applicable to this case, in part because the area of the electrodes is very small and it is no longer true that $A \gg H^2$. For a quantitative study of these systems we would need to account for edge effects.

In our study we assumed that there are only two kinds of alignment: parallel and perpendicular. In principle other kinds of behavior might be observable. In particular there is the classical Helfrich−Hurault instability which occurs for a smectic placed between two plates.[20] In this case the lamellae undulate but on average remain parallel.[21] This kind of instability should occur between the parallel and perpendicular morphologies.

We concentrated in this paper upon the equilibrium states of the sample. We ignored the kinetics, which in practice are very slow. How the system changes between states is best studied either by experiment or by simulation. We have said nothing in this paper about the frequency of the applied field. For samples of liquid crystals (used in displays) charge injection can be a problem and can cause flow effects. This is usually avoided by the use of a high-frequency alternating field. If this were done in the case of diblock copolymers, our calculations would still be valid because only the square of the field enters any of the equations.

Acknowledgment. G.G.P. and D.R.M.W. acknowledge support from an ARC Large Grant, and D.R.M.W. is supported by an ARC QEII.

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MA9908200