# Equilibrium Properties of a Diblock Copolymer Lamellar Phase Confined between Flat Plates

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We study theoretically the equilibrium behavior of the lamellar phase of an $A$-$B$ diblock copolymer melt. Each lamellar layer is an $A$-$B$,$B$-$A$ repeat unit and $n$ such layers are confined between, and parallel to, two identical flat plates. We find that the configurations with a half-odd-integer number of layers occur only when the difference between the two polymer-plate surface tensions is small, and then only below some critical plate separation. We calculate the discontinuity in the pressure at the transition point between two different values of $n$.

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Certain diblock copolymers are known to self-assemble spontaneously in the melt to form two-dimensional lamellae [1]. Each lamellar layer consists of polymers which are partially stretched in the $z$ direction (say) while the layer itself is liquid and retains translational symmetry in the $x$-$y$ plane. The self-assembly is driven by the immiscibility of the two chemical components of the polymer, denoted $A$ and $B$. By forming a lamellar phase the system minimizes the number of $A$-$B$ contacts, thereby saving energy which offsets the corresponding loss of polymer entropy. In a system containing lamellar layers a "stack" is formed in which the layers pile up alternately $A$-$B$, $B$-$A$, $A$-$B$, etc. This phase is a macromolecular analog of the lyotropic smectic-$A$ phases of liquid crystals. These copolymer systems have been the subject of much recent experimental [2–7] and theoretical interest [8–10]. Some of these experiments [2–4] have studied frustration in thin copolymer films at a substrate. When the film thickness is other than an integer (or half-integer) multiple of the lamellar thickness, "islands" or "holes" are observed in the uppermost layer. It has been suggested recently [11] that these surface structures may even appear when the film thickness is "happy," provided the air-$A$ and air-$B$ surface tensions are different and the "wrong" one is prepared at the upper surface (in this case there is no significant change in elastic energy). Frustration in thin copolymer films is also the subject of the present work, although here the film is confined between *two* plates. The effects of confinement on systems containing surfactant bilayers has also been investigated experimentally [12], although these are somewhat different from the copolymer lamellae that we consider here.

We study theoretically the equilibrium behavior of an $A$-$B$ diblock copolymer melt which is confined between two identical flat plates. Each polymer has a total degree of polymerization $N$ [13] and a monomer size $b$. We discuss the case where a fixed volume of polymer is confined between two infinite plates. The situation where the plates have finite size, and a reservoir of polymer is present, is rather similar but will not be discussed here. We also restrict our attention to the strong segregation limit (for temperatures well below the ordering temperature, but above the glass transition) and assume that the lamellar ordering occurs parallel to the plates. There is now strong evidence to suggest that this type of surface-induced ordering does indeed occur [5,6]. One lamellar layer is defined to be an entire $A$-$B$, $B$-$A$ repeat unit. The number of such layers between the plates $n$ is either an integer $\mathbb{Z}$ or half-odd-integer $\mathbb{Z}+\frac{1}{2}$. Configurations ("states") consisting of an integer number of layers will be referred to as "symmetric" and those with a half-odd-integer number of layers as "antisymmetric."

Three important parameters in our model are $\gamma_{AS}$, $\gamma_{BS}$, and $\gamma_{AB}$. The first two describe the surface tension between the $A$ polymer and the plate and the $B$ polymer and the plate, respectively, while $\gamma_{AB}$ describes the surface tension at the $A$-$B$ interface. Each of these surface tensions is dimensionless, in units of $k_BT/b^2$. We choose $\gamma_{AS} \leq \gamma_{BS}$, without loss of generality. Thus if the $A$ polymer resides next to only one of the plates the system is in an antisymmetric state, while if it resides next to both plates the system is symmetric.

In a bulk sample (no plates) the equilibrium layer thickness $L^*$ (in units of $b$) is determined by a simple balance between the elastic stretching energy of the polymers and the surface tension which acts at the $A$-$B$ interface [14]. Assuming that each polymer terminates at the lamellar surface and that adjacent layers do not significantly interpenetrate [15] we may estimate the elastic energy per polymer as $F_{\mathrm{el}}=(k/2N)(L/2)^2$, where $L$ is the layer thickness in units of $b$, and $k/N$ can be thought of as the entropic "spring constant" of the polymer ($k=3$ for a Gaussian chain). The energy associated with the $A$-$B$ interface is merely $F_{AB}=2N\gamma_{AB}/L$ per polymer. Minimization of $F=F_{\mathrm{el}}+F_{AB}$ then determines the equilibrium (bulk) layer thickness $L^*=(8\gamma_{AB}/k)^{1/3}N^{2/3}$, corresponding to a minimum free energy per chain $F(L^*)=3(k\gamma_{AB}^2/8)^{1/3}N^{1/3}$. In what follows it is convenient to express all lengths in units of $L^*$ and all energies in units of $F(L^*)$.

We now return to the case where the lamellar phase is confined between two infinite plates. By including the interaction between the polymer and the plate surfaces, as well as the terms $F_{\mathrm{el}}$ and $F_{AB}$, we obtain the total free energy per polymer $\mathcal{F}$, in units of $F(L^*)$:

$$\mathcal{F}(n,d)=\frac{1}{3}\left[\left(\frac{d}{n}\right)^2+\frac{2n}{d}+\frac{1}{d}\left(2\Gamma+\delta\frac{1-(-1)^{2n}}{2}\right)\right].$$

Here $\Gamma=\gamma_{AS}/\gamma_{AB}$, $\delta=(\gamma_{BS}-\gamma_{AS})/\gamma_{AB}$, $d$ is the plate separation in units of $L^*$, and we have used the identity $d=nL/L^*$ to eliminate the lamellar thickness as a parameter. Since the constant $k$ does not appear explicitly in this expression the discussion that follows is independent of the prefactor in $F_{\text{el}}$. Note that we have neglected the effect of the polymer-air interface which exists at the edge of the sample, with an associated surface tension $\gamma_{\text{air}}$. This is appropriate provided the sample is thin enough, $d \ll L^*(\gamma_{AS}/\gamma_{\text{air}})^{2/3}(V/\pi)^{1/3}$, where $Vb^3$ is the volume of the sample. Similarly we have assumed that the polymer remains in contact with the plates. For this to be the case the ratio $\gamma_{\text{air}}/\gamma_{AS}$ need only be slightly greater than unity (experimentally $\gamma_{\text{air}}/\gamma_{AB}$ might typically be of order 10). We will now minimize $\mathcal{F}$ to find the equilibrium number of layers $n(d)$ and thereby $\mathcal{F}(d)$. Since the system is quantized ($n$ is quantized) we cannot merely minimize $\mathcal{F}$, treating $n$ as a continuous variable. Instead we seek to determine $n(d)$ by calculating the points at which there is a transition from one value of $n$ to another. This occurs when the energies of the two states ($n$ values) coincide. We first determine the plate spacing $d_1$ at which the energies of the $n$ and $n+1$ states coincide. Solving $\mathcal{F}(n,d_1)=\mathcal{F}(n+1,d_1)$ we find

$$d_1=[2n^2(n+1)^2/(2n+1)]^{1/3}.$$

We next find the plate spacing $d_2$ at which the energies of the $n$ and the $n+\frac{1}{2}$ states coincide. Solving $\mathcal{F}(n,d_2)=\mathcal{F}(n+\frac{1}{2},d_2)$ we find

$$d_2=\{n^2(n+\tfrac{1}{2})^2[1+\delta(-1)^{2n}]/(n+\tfrac{1}{4})\}^{1/3}.$$

When $\delta>1$ there exists no real, finite $d_2$ for the antisymmetric states ($n\in\mathbb{Z}+\frac{1}{2}$). This indicates that only the symmetric states occur for $\delta>1$.

We now determine for what values of $d$ the antisymmetric states are accessible and when it is only the symmetric states which occur. We do this by determining the sign of the free energy difference, $\Delta\mathcal{F}=\mathcal{F}(n+\frac{1}{2},d_2(n))-\mathcal{F}(n+1,d_2(n))$, for a general symmetric state. This procedure determines whether the $n+1$ or the $n+\frac{1}{2}$ state is energetically preferable at the point at which a transition from the $n$ to the $n+\frac{1}{2}$ state *may* occur. When $\Delta\mathcal{F}<0$ both the symmetric and the antisymmetric states are accessible, otherwise only the symmetric states exist. Using our expressions for $\mathcal{F}$ and $d_2$ we find

$$\Delta\mathcal{F}=\frac{1+\delta}{3d_2}\left[\frac{n^2(n+\frac{3}{4})}{(n+1)^2(n+\frac{1}{4})}-\frac{1-\delta}{1+\delta}\right].$$

We may now solve $\Delta\mathcal{F}=0$ to find the critical value $n^*\in\mathbb{Z}$. For $n<n^*$ the antisymmetric states occur; otherwise only the symmetric states exist. In order to take account of the discrete nature of $n^*$ we introduce a real, continuous variable $m$, which is the solution to $\Delta\mathcal{F}(m)=0$ (a cubic equation in $m$, with only one positive root). We then have $n^*=\text{Int}[m]+1$, where $\text{Int}[m]$ is the largest integer less than or equal to $m$. For $\delta\ll 1$ we find $m=3/4\delta+O(1)$. Hence $m$ diverges as $\delta\to 0$; in this limit there is no energetic penalty associated with the antisymmetric states. For $\delta>0$ we observe that $m$ is monotonically decreasing with $\delta$, reaching zero at $\delta=1$. For $\delta>1$ only the symmetric states occur [16]. We define $d^*=d_2(n^*-\frac{1}{2})$ to be the plate separation below which antisymmetric states exist. A plot showing the variation of $d^*$ with $\delta$ is shown in Fig. 1.

We now have a complete description of the equilibrium conformation of the system. We find that the number of lamellar layers is given by

$$n=(\text{Int}[\alpha d]+\beta)/\alpha,$$

where $\alpha=1+\Theta(d^*-d)$, $\beta=\Theta(d_\alpha(\text{Int}[\alpha d]/\alpha)-d)$, and $\Theta(x)$ is the usual $\Theta$ function: $\Theta(x)=1$ if $x>0$, and otherwise $\Theta=0$. To see how this expression for $n$ is obtained consider the following: $n$ depends on whether $d$ is above or below the transition point between two states (one state where the layers are slightly compressed and one where they are slightly expanded). The term $\beta$ takes the position of this transition into account. The other term $\alpha$ takes care of whether the number of layers changes in integer or half-integer steps. The above results, combined with our expression for the free energy, determine the free energy as a function of the plate separation $d$. A plot of $\mathcal{F}(d)$ is shown in Fig. 2.

We may now calculate directly the scaled pressure $\Pi=\partial\mathcal{F}/\partial d$ using the above results and our expression for the free energy $\mathcal{F}$. Thus we adopt the convention that a positive pressure acts to reduce the plate separation. We are particularly interested in the behavior of $\Pi$ near a transition point, where the number of layers changes. We define $\Pi^-(n)$ to be the pressure exerted by the $n$-layer

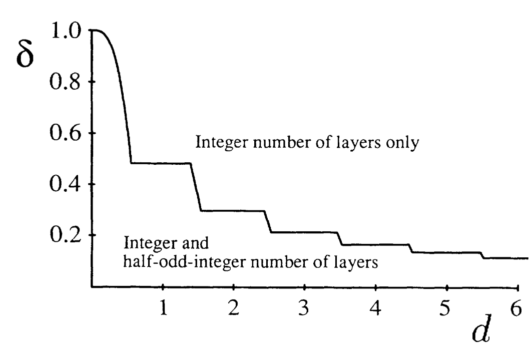

FIG. 1. Plot showing two different regions in the $d$-$\delta$ plane. In the upper region only those conformations with an integer number of layers exist, while in the lower region, close to the $d$ axis, conformations with a half-integer number of layers occur.

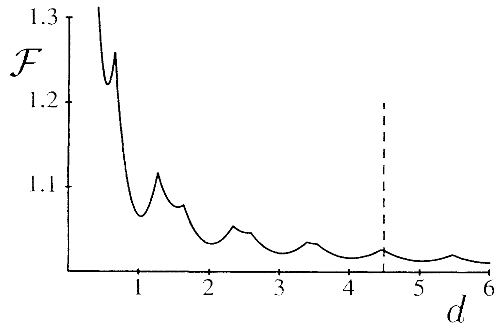

FIG. 2. The scaled free energy per polymer $\mathcal{F}$ as a function of the plate separation $d$ for the values $\delta=0.15$ and $\Gamma=0.1$. The cusps in $\mathcal{F}$ correspond to the transition points where the number of layers changes. There is a discontinuity in the pressure at these points. The value of $d^*$, below which the antisymmetric states exist, is shown by a vertical dashed line.

state when the plate separation $d$ is marginally below the transition point. For slightly larger values of $d$ a state with a greater number of layers is energetically preferable and the pressure is written $\Pi^+(x)$. The magnitude of the discontinuity in the pressure at the transition point is $\Delta\Pi=\Pi^- - \Pi^+$. It is also possible to show that a local minimum in the free energy exists if and only if $\Pi^-(n)>0$.

In what follows we will calculate the variation of $\Delta\Pi$ with $n$. We consider first the case $n>n^*$ where only the symmetric states occur. Using $\Pi^-(n)=\Pi(d_1(n),n)$ and $\Pi^+=\Pi(d_1(n),n+1)$ we find

$$\Delta\Pi(n)=2/d^2 .$$

We now turn to the other case $n<n^*$, where $\Pi^-(n)=\Pi(d_2(n),n)$, $\Pi^+(n)=\Pi(d_2(n),n+\frac{1}{2})$, and both the symmetric and the antisymmetric states occur. We first consider the case where the system changes from a symmetric to an antisymmetric state, in which case $N\in\mathbb{Z}$, and $\Delta\Pi$ is given by

$$\Delta\Pi=(1+\delta)/d^2 .$$

Finally we consider the case where the system changes from an antisymmetric to a symmetric state. In this case $n\in\mathbb{Z}+\frac{1}{2}$, and we find

$$\Delta\Pi=(1-\delta)/d^2 .$$

As $\delta\rightarrow 1$ the discontinuity in the pressure vanishes for the antisymmetric to symmetric transitions. This is to be expected since a discontinuity in the pressure signifies the existence of a transition and such transitions are now known to be absent for $\delta>1$.

It should be possible to study systems, like the one considered here, using an atomic force machine. In this case the pressure $\Pi$ may be measured as a function of the plate separation. Discontinuities in the pressure signify a change in the number of layers present and a direct comparison with our predictions may be possible. Note that in the present work we have been concerned with equilibrium properties only and have therefore not attempted to describe the dynamic processes involved in either creating or removing a layer. The creation of a new layer requires at least a local disruption of the lamella order. This allows material to pass to the new layer, which may grow by the propagation of an edge dislocation away from the disrupted region. The finite activation energy for this process will result in some hysteresis between compression and expansion of the plates. For thin samples, with a large volume, this activation energy may turn out to be small. This is because the size (and energy) of the disrupted region might be expected to remain roughly constant while the maximum energy of an edge dislocation scales like the sample size and all other terms in the energy are much larger, since they scale like the sample area. Finally note that the equilibration time after a change in $n$ may be rather long.

In summary we have determined the configuration adopted by a copolymer lamellar phase when it is confined between two flat plates. We have calculated both the free energy as a function of the plate separation and also the discontinuity in pressure $\Delta\Pi\sim d^{-2}$ at the transition point, where the number of layers in the system changes.

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[15] It has been suggested that two grafted polymer brushes compressed against one another do not significantly interpenetrate [P. G. de Gennes, C. R. Acad. Sci. (Paris) **300**, 839 (1985)]. Here also it seems reasonable to neglect interpenetration since a lamellar layer is merely an "equilibrium polymer brush."

[16] This is identical to the criterion for complete wetting of the interface between a solid surface and $B$ polymer by a droplet of $A$ polymer, which also occurs for $\delta < 1$.