Interfacial profiles of mismatched lamellae in thin diblock copolymer films
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I. INTRODUCTION

Symmetric diblock copolymers, in the strong segregation limit (SSL), are known to microphase separate into lamellae with a distinct equilibrium spacing—$L_b$. This spacing has been shown to be theoretically\(^1\) given by

$$L_b = \left( \frac{12 \gamma_{AB}}{\pi^2 k_B T} \right)^{1/3} N^{2/3},$$

where $N$ is the number of monomers on the chain, each of size $a$, and $\gamma_{AB}$ is the $AB$ interfacial tension. This scaling relation has been confirmed experimentally for symmetrical diblocks in the SSL.\(^2\) Although lamellae are predicted to form for these block copolymers, this occurs only on a (relatively) local scale, i.e., of the size of a few lamellae. On a more global scale various defects disrupt the local lamellae pattern leading to a globally unaligned sample. To make use of their natural inherent nanoscale lamellae morphology, for example in such applications such as lithographic templating, it is important to control these lamellae patterns on a global scale. This is where, currently, a significant amount of research is focused.

One method of aligning block copolymer melts is to place the melt in a thin film geometry, i.e., on a flat substrate. If the substrate and upper free surface favors one of the blocks over the other (which is likely) and the thickness of the thin film is an integer multiple of $L_b$, lamellae will form parallel to the confining surface. When the thickness of the film is not an integer multiple of the lamellar spacing, the system is frustrated. This is because the lamellae cannot achieve their equilibrium spacing. One way for the system to relieve this frustration, if the top surface is free, is for island/holes to form in the uppermost layer. In this scenario, the film will vary in thickness and the difference will be equal to $L_b^2$.

By controlling the wetting properties of the blocks with the bottom surface it is possible, using the island/holes phenomena, to produce a distinct surface topography at the top (free) surface of the thin film (see Fig. 1). To do this consider the following. A substrate is produced such that stripes of width $w$ alternate across the entire substrate, and can be “tuned” so that one stripe favors the $A$ block (for example) and the other stripe favors the $B$ block. This can be done quite accurately experimentally using procedures such as shown by Rockford et al. and discussed subsequently.\(^3\)-\(^13\) Consider now the case where $w \gg L_b$. If the film thickness is not exactly an integer multiple of $L_b$ and assuming the upper surface (air) prefers one of the blocks, at the top surface a ridge-like structure will form (see Fig. 1) where we get symmetrical wetting in one set of stripes and in adjacent stripes we get asymmetrical wetting. The height of the steps are then $L_b$. At the boundary between symmetrical and antisymmetrical regions the lamellae are mismatched, i.e., $A$ blocks adjoin $B$ blocks and vice versa. In the SSL the system pays a large surface energy penalty for this morphology. The question therefore is how exactly do these regions match up?

Another scenario that can occur is if one set of stripes are tuned to be neutral and the top surface (air) is also neutral, with respect to each block. In this case if the average film thickness is not an integer multiple of $L_b$, a morphology of parallel symmetric lamellae, adjacent to perpendicular lamellae should form. Once again the question arises as how these mismatched regions join.

The last scenario we shall investigate is the case where the stripes alternate in affinity for $A$ and $B$ blocks, and the top surface is neutral. If the film thickness is an integer multiple of the lamellar spacing, parallel lamellae should be induced...
but with blocks alternating at the surface. Thus once again at the stripe boundaries a mismatch region occurs, and we ask what is the nature of the lamellar morphology in this region.

There have been several studies of how two different mismatched grains join at an interfacial boundary. The works by Gido et al.,14–17 Schick and co-workers,18,19 Matsen20 and Winey and co-workers21–23 are important examples. In these studies three primary types of joins between grain boundaries have been identified. These are T junctions, in which the two lamellar grains intersect perpendicularly. In this case the continuity of one phase is disrupted. This phase then forms semi-circular caps at the boundary. The second type of join is a chevron boundary where the lamellar grains intersect at some (small) angle. In this case both phases are continuous across the kink. Finally an Ω boundary, which occurs when the lamellar grains intersect at a large angle, has been observed. Here a protrusion appears in the kink, which is a result of the large bending penalty the lamellar would pay if they took on a chevron formation. In all these works many lamellar layers are present, so that we are in a “bulk” type medium. The situation discussed in this paper is different because we have substrates present which not only impose confinement effects on the lamellar layers, but also disrupt the bulk type lamellar pattern. This alters the possible morphologies that may appear in the adjoining regions.

The present study differs from previous studies of block copolymers on patterned surfaces3–13 since we consider the case $w \gg L_h$. This results in parallel lamellae forming in each stripe and due to the different wetting conditions the lamellae in adjacent stripes are mismatched. We investigate the morphology of this mismatched region. However this system is very new and experimental work on it is very preliminary. Thus comparison with experiments is limited. We note, recently there has been some work on polymer blends near patterned surfaces.24,25 However the physics of blends is recently there has been some work on polymer blends near patterned surfaces.24,25 However the physics of blends is

![Diagram](https://via.placeholder.com/150)

**FIG. 1.** Schematic of island/hole system, from side on. Patterned surface is at bottom, black stripes favor one block, white stripes the other block. Here $n = 1, 2, 3, \ldots$

In investigations of these kinds of systems one is hampered, to a certain degree, by the complexity of the possible morphologies that may arise. Many theoretical techniques rely on the fact that one knows a set of certain possible morphologies and then one minimizes the free energy of the system with respect to these morphologies. The actual observed morphology is then that state which has the minimum free energy of the whole set. This process works well when one knows the precise morphology of the system. For our investigation, such an analysis is not useful because the morphology in the adjoining regions may be irregular and is something that is not known a priori.

A much more powerful (and appropriate) technique for investigating such problems is a phenomenological approach where one directly numerically integrates the dynamical evolution equation. Such a technique has been applied with success to confined thin film block copolymer problems by Chakrabarti and co-workers.12,26,27 This coarse grained model for block copolymers is based on a Cahn–Hilliard model initially formulated to study ordering in binary fluid mixtures. In this model the free energy is a function of the order parameter $\Phi(r, t) = \rho_1(r, t) - \rho_0(r, t)$, where $\rho_i$ is the density of the $i$th component. The free energy is then

$$F[\Phi(r, t)] = \frac{1}{k_B T} \int_V d\mathbf{r} \left[ \frac{b}{2} \Phi^2 + \frac{u}{4} \Phi^4 + \frac{K}{2} (\nabla \Phi)^2 \right]$$

$$+ B \int_{V'} d\mathbf{r}' G(\mathbf{r}, \mathbf{r}') \Phi(\mathbf{r}, t) \Phi(\mathbf{r}', t)$$

$$- \frac{F_{\text{surface}}}{k_B T},$$

where $F_{\text{surface}}$ is the surface energy contribution and $V$ is the volume of the system. The parameters $b, u, K$ and $B$ are related to polymer size etc.12 $G$ is the Green’s function satisfying $\nabla^2 G = -\delta(\mathbf{r} - \mathbf{r}')$. The free energy is a functional of $\Phi$, which in turn is defined at any point $\mathbf{r}$ in space and at time $t$. To proceed we need to discretize space and thus we consider a rectangular three dimensional (3D) lattice with the striped surface in the $x$–$y$ plane. Stripes have infinite length and run parallel to the $y$ axis. The film has a finite thickness, in the $z$ direction.

Initially we consider a contact potential for the surface-diblock energy and so $F_{\text{surface}}$ is given by

$$F_{\text{surface}} = \int_V d\mathbf{r} \left[ h(x, y) \delta(z) \right] \Phi(x, y, z, t).$$

The surface potential is given by

$$h(x, y) = \begin{cases} h_{\text{even}} & \text{for } 2n w \leq x \leq (2n + 1) w, \\ h_{\text{odd}} & \text{for } (2n + 1) w \leq x \leq (2n + 1) w, \end{cases}$$

where $n = 0, 1, \ldots$. In general we will consider only one set of stripes, since the pattern is repeated over the other stripes.
Eq. (3), \( h_{\text{odd}} \) and \( h_{\text{even}} \) are constants over the stripe width. For different cases we set \( h_{\text{odd}} \) and \( h_{\text{even}} \) to get the desired wetting conditions.

We have also considered a long-range surface interaction potential in our studies. In this case, the surface free energy is taken to be

\[
F_{\text{surface}} = \int_V d\mathbf{r} [h(x,y,z)] \Phi(x,y,z,t),
\]

where

\[
h(x,y,z) = h(x,y)|\varepsilon|^\sigma \quad \text{for } z > 0,
\]

and

\[
h(x,y) = \begin{cases} h_{\text{even}} & 2n_w \leq x \leq (2n + 1)w \\ h_{\text{odd}} & (2n + 1)w \leq x \leq 2(n + 1)w. \end{cases}
\]

At \( z = 0 \) the surface potential is taken to be either \( h_{\text{even}} \) or \( h_{\text{odd}} \). We have considered \( \sigma = 3 \) and \( \sigma = 4 \) in our studies.

Now to determine how the system evolves to equilibrium, below the order–disorder transition, we use the Cahn–Hilliard equation

\[
\frac{\partial \Phi}{\partial t} = M \nabla^2 \mu,
\]

where \( M \) is the mobility and \( \mu(\mathbf{r}) \) is the chemical potential at the point \( \mathbf{r} \). To determine \( \mu \) we take the functional derivative of the free energy [Eq. (1)] with respect to the order parameter. Thus applying the operation \( M \nabla^2 (\partial F/\partial \Phi) \) to Eq. (1) and rescaling, as done by Chen and Chakrabarti,\textsuperscript{12} we obtain the following equation in dimensionless form:

\[
\frac{\partial \Phi}{\partial t} = \frac{1}{2} \nabla^2 (-\Phi + \Phi^3 - \nabla^2 \Phi) - \alpha \Phi - \delta(z) \frac{\partial^2 h(x,y)}{\partial x^2} - \sqrt{\varepsilon} \eta(\mathbf{r},t).
\]

The last term on the right hand side of the above equation is a random noise term\textsuperscript{12} introduced to mimic the effect of thermal fluctuations. In practice it has an important effect in that it allows the system to escape from some metastable equilibrium states. The parameter \( \varepsilon \) is the magnitude of the fluctuations and is set here to 0.5. The distribution of \( \eta(\mathbf{r},t) \) is determined by the fluctuation–dissipation theorem i.e.,

\[
\langle \eta(\mathbf{r},t) \eta(\mathbf{r}',t') \rangle = -\nabla^2 \delta(\mathbf{r} - \mathbf{r}') \delta(t - t').
\]

Equation (8) is appropriately discretized and we use time steps of \( \Delta t = 0.001 \). The simulation begins at time \( t = 0 \) and Eq. (8) is iterated until a stable equilibrium solution is found, i.e., until there is no change in the order parameter. Initially \( \Phi \) is in a randomly disordered configuration.

Before proceeding to study the confined, thin film behavior of these diblock melts we consider the bulk equilibrium properties of this model. It has been shown by Brown and Chakrabarti\textsuperscript{16,27} that Eq. (8), without the surface term (i.e., the term involving the \( \delta \) function), with \( \alpha = 0.01 \) produces lamellae with a sinusoidal order parameter profile.\textsuperscript{12,26,27} Since the free energy is an expansion to fourth order, this theory is not quantitatively valid in the SSL, where the order parameter has a square-wave profile. However calculations for this model,\textsuperscript{12} with \( \alpha = 0.01 \) produce a \( \chi N \) of roughly 42 (\( \chi \)-Flory–Huggins interaction energy parameter), and so our results should be qualitatively valid in the SSL. This value of \( \alpha \) produces a bilayer spacing of 15 lattice sites or \( L_B = 7.5 \).

As has been mentioned above, Eq. (8) is discretized on a 3D cubic lattice. There is a hard wall at \( z = 1 \). Since the stripes run parallel to the \( y \) axis, we assume the profile does not vary in the \( y \) direction. This speeds up our computations as our study becomes two dimensional (2D) i.e., density varies in \( x - z \) plane. Making this study 2D seems reasonable on volume conservation grounds. In addition, since this is the first study of this system, to simplify things, we feel the simplification to 2D is appropriate. Thus we initially consider the lattice to have \( L \) lattice sites in the \( x \) direction and \( H \) lattice sites in the \( z \) direction. At the boundaries in the \( x \) direction (i.e., \( x = 1 \) and \( x = L \)) we impose periodic boundary conditions. The top surface can either be flat or can have an island/hole structure. If the top surface is flat it is treated similarly to the hard wall at \( z = 1 \). At these two boundaries we impose no flow perpendicular to the boundary, i.e., \( \partial \mu / \partial z = 0 \). To impose this condition we must define (ghost) lattice sites above \( z = H \) (i.e., at \( z = H + 1 \)) and below \( z = 1 \) (i.e., at \( z = 0 \)). Practically, this then implies that \( \Phi(x,1) = \Phi(x,0) , \Phi(x,H) = \Phi(x,H + 1) \), \( (\partial^2 \Phi(x,z) / \partial z^2) |_{z=1} = (\partial^2 \Phi(x,z) / \partial z^2) |_{z=0} \) and \( (\partial^2 \Phi(x,z) / \partial z^2) |_{z=H} = (\partial^2 \Phi(x,z) / \partial z^2) |_{z=H+1} \). Equation (8) is solved only at real lattice sites but when evaluating higher order derivatives of \( \Phi \), at boundary sites, the above equations are used. If the top surface is not flat but rather has a rectangular protrusion or island the boundary condition of no flow must be still implemented. This is done as detailed above for points other than corners. At corner points we must impose both \( \partial \mu / \partial z = 0 \) and \( \partial \mu / \partial x = 0 \).

III. MORPHOLOGY

The first case we shall consider is where the top surface is flat. This will occur if there is no preference for either block at the air interface. Alternatively this could occur if the interfacial tension of air with both blocks is large. We initially consider the thickness of the film to be one bilayer. Thus well away from the stripe boundaries, lamellae parallel to the substrate should form. We use a 120x15 lattice so that exactly one bilayer fits parallel to the substrate. The size of a stripe is 60 lattice spacings and we set \( h_{\text{odd}} = -h_{\text{even}} = 0.4 \). This stripe of the patterned surface favors the \( A \) block as much as the other stripe favors the \( B \) block. Figure 2(a) shows the lamellar pattern that forms for this case. Well away from the stripe boundaries at \( x = 30 \) and \( x = 90 \), parallel lamellae form. In the adjoining region one of the phases gets cut off, leaving the other phase to have continuity at the boundary. The lamellar pattern is somewhat similar to what would occur in a kink boundary (chevron pattern).\textsuperscript{22} However because of the presence of the two confining surfaces, both phases cannot have continuity through the kink.

To see how good our assumption about the replication of the lamellar pattern over stripe is, we carried out another run where the size of the system was increased to a 240x15 system, so that we have four stripes across the lattice. The resulting morphological pattern is shown in Fig. 2(b). It is
clear that morphologies are replicated. The important point to note is that at the boundary between stripes one phase keeps continuity while the other phase is cut off. This allows the system to reduce the $AB$ interfacial energy, but at the cost of some bending energy.

We next consider the effect of increasing the film thickness on the morphological pattern. We use a $120\times 30$ lattice so that the film is two bilayers thick. The resulting morphological pattern is shown in Fig. 2(c). In the bilayer adjacent to the patterned surface the lamellar pattern is similar to the case where the film thickness is one bilayer spacing. In the second bilayer the pattern becomes more complicated. Well away from the stripe boundaries, the lamellae attempt to form lamellae parallel to the substrate. However near the stripe boundaries, because the lamellae bend, to reduce the $AB$ interfacial area, perpendicular lamellae form. This state actually is a long-lived metastable state, as our runs with longer-range potential confirm.

In Figs. 2(d) and 2(e) we show morphology of a thicker film for a long-range interaction potential with $\sigma = 3$. The system size here is $128\times 32$ and the noise strength is 0.2. In Fig. 2(d) the system is quenched directly to this low-temperature state from a high-temperature disordered state. Note the formation of perpendicular lamellae near the upper surface [similar to the case of Fig. 2(c)]. However, when we cool the system slowly starting from a noise strength of 0.8 till we reach the final low temperature of interest, the defects seen in Fig. 2(d) get ironed out by this annealing process. The resulting morphology of well-defined parallel lamellae is shown in Fig. 2(e). A similar, almost identical morphology is obtained with $\sigma = 4$.

Let us consider now the more experimentally relevant situation where the top surface (air) prefers one of the blocks over the other and so an island/ hole formation results. In one of the stripes we will get symmetric wetting, i.e., the same block will be found at the substrate and top surface, while in the other stripe asymmetric wetting will occur. To obtain the appropriate condition for such a situation we consider a lattice $240\times 15$ with an additional rectangular layer of dimensions $120\times 7$ at the top [see Fig. 3(a)]. The fact that one phase is favored at the top surface (air), induces parallel lamellae to form through the thin film melt. The joining of the lamellae near the stripe boundary has a similar morphology to that found in Fig. 2(a). In the layer directly adjacent to the striped surface, only one phase has continuity at the boundary. However in the next layer, both phases keep their continuity through the boundary. In Fig. 3(b) we have increased the film thickness so that two bilayers can form. The pattern in the join region is exactly the same as in Fig. 3(a).

The bending of the lamellae through the kink region reduces the $AB$ surface area, but at the cost of stretching energy of the chains and bending of the lamellae. The overall lamellae profile in the kink region therefore represents the optimal configuration for diblocks in the SSL. In Sec. IV we shall discuss this profile in more detail.

The last case we consider is where we have a striped surface, with one stripe favoring one block and the other stripe is neutral. The top surface is neutral as well and the film thickness is allowed to vary. Thus in the neutral stripe perpendicular lamellae form while in the other stripe parallel lamellae form. The thickness in the parallel lamellae region is $L_b$, while in the neutral stripe the film thickness is slightly greater than one lamellar spacing. Once again the joining of

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**FIG. 2.** (a) Density profile for $120\times 15$ lattice, with stripes of length 60 units. White corresponds to $A$ blocks and black to $B$ blocks. (b) Same as (a) except we increase system to a $240\times 15$ lattice. Note that in the join region of (a) and (b) the kink has a similar form. (c) Same as (a) except system’s size is $120\times 30$. (d) Deep quench with a long-range surface interaction potential for a system size of $128\times 32$. (e) Same as in (d) except the system here has been slowly cooled to the low temperature state starting from a high-temperature phase.

**FIG. 3.** (a) Density profile in the island/ hole setup where we consider a $240\times 15$ lattice and an additional $120\times 7$ rectangle at the top, with stripes of length 120 units. (b) Density profile in the island/ hole setup where we consider a $120\times 30$ lattice and an additional $60\times 7$ rectangle at the top, with stripes of length 60 units.

**FIG. 4.** Density profile for a system of size $120\times 15$ and extra rectangular region of size $120\times 5$ at the top, with stripes of length 60 units. One stripe is neutral to both blocks.
the two regions is investigated. Figure 4 shows that well formed perpendicular and parallel lamellae are formed well away from the stripe boundary. In the adjoining region it appears that the optimal formation of the lamellae for each phase is attempting to keep its continuity. The interfacial region between parallel and perpendicular lamellae is similar to a T junction\footnote{G. G. Pereira and D. R. M. Williams, Macromolecules \textbf{31}, 5904 (1998).} found previously. However the difference here is that both blocks (black and white) attempt to preserve their continuity through the boundary. This is due to the thin film geometry.

IV. KINK–LAMELLAR PROFILE

If we examine the figures (especially Figs. 2 and 3) we see a fairly clear kink formed in the first complete bilayer and in all subsequent bilayers. This kink joins two regions of the bilayer separated by a vertical distance $L_b$. It has a characteristic length $L_{\text{kink}}$ in the horizontal direction. This length is normally much smaller than the stripe width and is of the same order as the lamellar spacing. One obvious question is what determines the size of the kink? This kind of question arises very often in condensed matter physics particularly in the study of magnetism and liquid crystals. The general approach used in these topics is to write down the free energy of the system with some boundary conditions specified at $x = \pm \infty$ and then minimize it. The free energy usually consists of two kinds of terms. The first is a bending term, which favors a slowly varying solution and hence a large $L_{\text{kink}}$. The second is a restoring term, which favors a sharp kink and a small $L_{\text{kink}}$. The balance of these two terms gives a length scale which is $L_{\text{kink}}$. If we try and apply this kind of approach to our system by using a smectic free energy we find that there is no restoring term, i.e., all terms in the free energy tend to extend the kink and make it less sharp.

This kind of approach thus does not work for our system. The reason is fairly clear. The confinement of the first continuous bilayer is present not only at $x = \pm \infty$, but throughout the entire length of the bilayer. In some cases this confinement is due to the surface, while in other cases it is due to the surrounding lamellae. The bilayer is thus confined in a “stepped pipe” as shown in Fig. 5. In either case, it is the geometry of the confinement which controls the size of the kink. This geometry imposes that the kink be of the size of the lamellar spacing, which is what we find.

An additional complication arises in this system due to the fact that disordering can take place due to externally imposed confinement and distortion of the lamellae. This is very clear in Fig. 3(a), where in the middle of the kink the width of the layer decreases, and more gray ($\Phi = 0$) is found. This implies that the diblocks are disordering within the kink. This is not very surprising—the lamellae clearly pay a significant bending penalty within the kink. One way of avoiding this penalty is to disorder. Of course this process also involves some penalty.

V. CONCLUSION

In this paper we have examined the morphology of symmetric diblocks in the region between two stripes. We can make some fairly general conclusions regarding the typical structures which are likely to be seen. The most basic conclusion is that across a stripe boundary the favored morphology is to form a kinked lamella. This allows only one of the phases to be continuous, but does prevent a large interfacial energy penalty which would occur if both phases were discontinuous. The kink is fairly small (i.e., sharp), and has the same length scale as the lamellar thickness. These kinks are most regular in the case where the upper surface has a step. This is the usual case experimentally.

In the case where the upper surface is forced to be flat, the morphology can be more complicated. Kinks are found near the lower (striped) surface, where the lamellae are parallel to the substrate. However, in the region near the upper surface perpendicular lamellae can be found and the morphology becomes obscure for a deep quench. These defects can, however, be ironed out by starting from a high temperature phase and slowly cooling the system to the desired low temperature of interest. This might be of experimental interest as a method to prepare a sample with well-defined lamellae and fewer defects.

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