Motion of a transverse/parallel grain boundary in a block copolymer under oscillatory shear flow

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Abstract

A mesoscopic model of a diblock copolymer is used to study the motion of a grain boundary separating two regions of perfectly ordered lamellar structures under an oscillatory but uniform shear flow. The case considered is a grain boundary separating lamellae along the so called parallel orientation (with wavevector parallel to the velocity gradient direction) and along the transverse orientation (wavevector parallel to the shear direction). In the model considered lamellae in the parallel orientation are marginal with respect to the shear, whereas transverse lamellae are uniformly compressed instead. A multiple scale expansion valid in the weak segregation regime and for low shear frequencies leads to an envelope equation for the grain boundary. This equation shows that the grain boundary moves by the action of the shear, with a velocity that has two contributions. The first contribution, which arises from the change in orientation of the grain boundary as it is being sheared, describes variations in monomer density in the boundary region. This contribution is periodic in time with twice the frequency of the shear and, by itself, leads to no net motion of the boundary. The second contribution arises from a free energy increase within the bulk transverse lamellae under shear. It is also periodic with twice the frequency of the shear, but it does not average to zero, leading to a net reduction in the extent of the region occupied by the transverse lamellae. We find in the limit studied that the velocity of the grain boundary can be expressed as the product of a mobility coefficient times a driving force, the latter given by the excess energy stored in the transverse phase being sheared.
1 Introduction

Self-assembly of block copolymers is one possible route to the development of nanostructured materials, either directly or as templates. The major challenge that needs to be overcome for widespread application of these materials is the development of long ranged order in the polymer over scales much larger than the wavelength of the mesophase. The purpose of this paper is to investigate the motion of a grain boundary, an extended topological defect separating two lamellar phases that exhibit long ranged order but along different directions. Our study is an extension of ref. [1] in that we explicitly consider here that the block copolymer is under an externally imposed, oscillatory and uniform shear flow. The study is motivated by the widespread use of both steady and oscillatory shear flows to induce long ranged order in lamellar phases.

The system under consideration is a symmetric diblock copolymer slightly below its order-disorder transition temperature $T_{ODT}$ (weak segregation regime). The equilibrium phase is a lamellar structure in which nanometer sized layers rich in A or B monomers alternate in space. When the copolymer is quenched from a high temperature to a temperature $T < T_{ODT}$, a transient polycrystalline sample results comprised of an ensemble of locally ordered grains but of arbitrary orientations. A large number of defects are present in the sample in addition to grain boundaries that include dislocations and disclinations.

Different methods of sample alignment are being investigated experimentally, including substrate induced patterning [2, 3, 4], step induced orientation of thin films [5], electric fields that take advantage of a non uniform dielectric constant [6, 7], or of the existence of ions in the copolymer [8], and oscillatory shear flows in bulk samples [9, 10, 11, 12, 13, 14]. We focus here on the latter case as there is no agreement at present on the issue of orientation selection as a function of the physical properties of the copolymer and the parameters of the flow. For the purposes of the discussion, three basic orientations of the lamellae relative to the shear flow are conventionally defined: parallel, in which the lamellar planes are parallel to the flow velocity; transverse in which the lamellar normal is parallel to the flow, and perpendicular in which the lamellar normal is parallel to the vorticity of the imposed flow. A review of current experimental phenomenology can be found in [15, 16].

In an attempt to clarify the existing phenomenology about orientation selection of lamellar phases, we recently undertook a theoretical stability analysis of such phases under oscillatory shear flows with and without viscosity contrast between the microphases [17, 18]. At fixed temperature, we found that there is a finite range of shear amplitudes within which periodic lamellar structures along a given direction exist. For amplitudes larger than a certain critical amplitude, the lamellar phase “melts” into a disordered phase, possibly reforming with a different orientation rel-
ative to the shear, the new orientation being within the band of allowed solutions. Lamellar configurations within the band of allowed solutions can in turn become unstable against long wavelength perturbations. The regions of occurrence of this secondary instability were given in refs. [17, 18] as a function of the orientation of the lamellae and the shear rate. Generally speaking, it was found that the region of stability of perpendicular lamellae is larger than that of parallel lamellae, and both considerably larger than the region of stability of the transverse orientation. Our results also showed that the critical mode of instability is typically along the perpendicular orientation, so that the decay of an unstable region of parallel or transverse lamellae would lead, at least initially, to lamellae predominantly oriented along the perpendicular direction. These results were interpreted through a geometric description of the lamellar distortion, suggesting that the emerging mode of instability is the one that causes the largest decrease in lamellar wavelength under shear. Finally, the results were shown to be fairly insensitive to viscosity contrast between the microphases.

While the results just summarized narrow the range over which particular orientations can be in principle observed experimentally, they do not provide an orientation selection mechanism among competing, linearly stable stationary states. We therefore turn our attention to dynamical aspects of the competition between coexisting orientations in a macroscopic sample, and to orientation selection mechanisms of dynamical nature. We focus in this paper on the motion of a front or boundary that separates two ordered regions of parallel and transverse orientations. Parallel lamellae in the mesoscopic description employed are marginal with respect to the shear, and therefore unaffected by the flow. Transverse lamellae, on the other hand, are compressed by the shear, a fact that is shown to induce boundary motion toward the region of transverse orientation. Therefore parallel lamellae are expected to become prevalent over transverse lamellae, even in those ranges of parameters of the polymer and of the flow in which transverse lamellae are linearly stable.

The role that topological defect motion plays on structure coarsening under shear flows has already been investigated numerically in [19, 20]. Either a density functional description ([19]), or a cell dynamical system model ([20]) have been used to study domain coarsening of an initially macroscopically disordered configuration. For steady shears, Zvelindovsky et al. [19] show that the shear is very effective in speeding up the formation of lamellar domains, and argue that the perpendicular orientation is most stable. Ren et al. [20] more specifically focused on topological defect motion and annihilation, and the amplitudes of the oscillatory shear necessary to eliminate them to form a perfectly ordered lamellar structure.
2 Mesoscopic model equation of a lamellar phase under shear

At a mesoscopic level, and for time scales that are long compared with the relaxation time of the polymer chain, a block copolymer melt is described by an order parameter $\psi(r)$ which represents the local density difference between the two monomers constituting the copolymer. The corresponding free energy was derived by Leibler in the weak segregation limit (close to $T_{ODT}$) \[21\], and later extended by Ohta and Kawasaki to the strong segregation regime \[22\]. If the temporal evolution of $\psi$ occurs through advection by a flow field as well as through local dissipation driven by free energy reduction, $\psi$ obeys a time dependent Ginzburg-Landau equation that in the symmetric case of equal volume fraction of the two monomers is given by \[23\],

$$
\frac{\partial \psi}{\partial t} + \mathbf{v} \cdot \nabla \psi = \nabla^2 \left( -\psi + \psi^3 - \nabla^2 \psi \right) - B\psi. \tag{1}
$$

All quantities have been made dimensionless, including the advection velocity $\mathbf{v}$, and the long range polymer interaction coefficient $B$. The order-disorder transition between a disordered phase ($\psi = 0$) and a lamellar phase ($\psi \neq 0$) takes place at $B_0 = 1/4$. For $B \gtrsim B_0$, $\psi$ is a periodic function of wavenumber $q_0 = 1/\sqrt{2}$.

The physical system under consideration here is a layer of block copolymer, unbounded in the $x$ and $y$ directions, and being uniformly sheared along the $z$ direction (Fig. 1). The layer is confined between the stationary $z = 0$ plane, and the plane $z = d$ which is uniformly displaced parallel to itself with a velocity $\mathbf{v}_{\text{plane}} = \gamma d \omega \cos(\omega t) \mathbf{\hat{x}}$, where $\mathbf{\hat{x}}$ is the unit vector in the $x$ direction.

We first briefly summarize the results of refs. \[17, 18\] concerning stationary lamellar solutions in shear flow. In the weak segregation limit $\epsilon = (B - B_0)/2B_0 \ll 1$, the solution for the monomer composition can be obtained perturbatively in $\epsilon$,

$$
\psi(r) = 2A(t) \cos(\mathbf{q} \cdot \mathbf{r}) + A_1(t) \cos(3\mathbf{q} \cdot \mathbf{r}) + \ldots \tag{2}
$$

where $A(t) \sim \mathcal{O}(\epsilon^{1/2})$, and $A_1(t)$ and higher order mode amplitudes are of higher order in $\epsilon$. We have defined $\mathbf{r} = x_1 \mathbf{\hat{x}} + x_2 \mathbf{\hat{y}} + x_3 (\gamma \sin(\omega t) \mathbf{\hat{x}} + \mathbf{\hat{z}})$, a vector that is expressed in a non orthogonal basis set which follows the imposed shear, and $\mathbf{q} = (q_1, q_2, q_3)$, the wavevector in the corresponding reciprocal space basis set $\{ \mathbf{g}_1 = \mathbf{\hat{x}} - \gamma \sin(\omega t) \mathbf{\hat{z}}, \mathbf{g}_2 = \mathbf{\hat{y}}, \mathbf{g}_3 = \mathbf{\hat{z}} \}$. Note that in this new coordinate system, the wavevector of a perfectly ordered configuration is stationary. Three orientations relative to the shear can be defined as follows: $q_3 \neq 0$, $q_1 = q_2 = 0$ is a purely parallel orientation, $q_2 \neq 0$, $q_1 = q_3 = 0$ is a perpendicular orientation, and $q_1 \neq 0$, $q_2 = q_3 = 0$ is a transverse orientation.

For constant viscosity and if we neglect flow induced by the lamellae themselves, the velocity field in the layer is independent of monomer composition, and is given
by,
\[ \mathbf{v} = \gamma \omega \cos(\omega t) \; z \; \hat{x}. \]  
To lowest order in \( \epsilon \), the amplitude \( A(t) \) satisfies the equation \[17\],
\[ \frac{dA}{dt} = \sigma[q^2(t)]A - 3q^2(t)A^3, \]  
with \( q^2(t) = q_1^2 + [\gamma \sin(\omega t)q_1 - q_3]^2 + q_2^2 \) and \( \sigma(q^2) = q^2 - q^4 - B \). This equation can be integrated to give the marginal stability boundaries, and the function \( A(t) \) itself \[17\]. From this analysis, a critical strain amplitude \( \gamma_c \) was identified, function of the orientation \( \mathbf{q} \) but independent of the frequency \( \omega \), such that for \( \gamma < \gamma_c \) the uniform lamellar structure oscillates with the imposed shear, but for \( \gamma > \gamma_c \) \( A(t) \) decays to zero; i.e., the lamellar structure melts, according to the terminology used by experimentalists.

The stability of this base lamellar pattern was then addressed by Floquet analysis. Regions of stability were obtained for lamellar solutions of arbitrary orientation, that were generally largest for orientations near the perpendicular direction, and smallest in the vicinity of the transverse direction. As discussed in the introduction, this stability analysis provides some guidance on the issue of orientation selection, but we wish to extend here the analysis of existence and stability to possible selection by dynamical mechanisms. The specific case considered in this paper is the motion of a grain boundary separating regions of uniform parallel and transverse orientations under oscillatory shear.

We use in what follows a different form of the equation governing the evolution of the monomer composition \( \psi \), known as the Brazovski equation (or Swift-Hohenberg equation in the fluids literature) \[24, 25, 26\]. Both this equation and eq (1) lead to the same amplitude or envelope equations near onset \[27, 28\], and hence lead to identical results in the limit addressed in this paper. The Swift-Hohenberg equation for a scalar order parameter is,
\[ \frac{\partial \psi}{\partial t} + \mathbf{v} \cdot \nabla \psi = \epsilon \psi - (\nabla^2 + q_0^2)^2 \psi - \psi^3, \]  
where all quantities are dimensionless. In this units \( q_0 = 1 \), although we will retain the symbol \( q_0 \) in the equations that follow for clarity of presentation.

As was the case in the analyses presented in refs. \[17, 18\], we introduce a new frame of reference in which the velocity vanishes. In the case of an imposed oscillatory shear of amplitude \( \gamma \) and angular frequency \( \omega \), we define a set of non-orthogonal coordinates \( x' = x - a(t)z \) and \( z' = z \) where \( a(t) = \gamma \sin(\omega t) \). We assume that the system is uniform in the third direction, and therefore simply focus on a two dimensional case. Equation (4) transforms to,
\[ \frac{\partial \psi}{\partial t} = \epsilon \psi - (\nabla^2 + q_0^2)^2 \psi - \psi^3, \]  
5
where

$$\nabla^2 = (1 + a(t)^2) \frac{\partial^2}{\partial x'^2} - 2a(t) \frac{\partial^2}{\partial x' \partial z'} + \frac{\partial^2}{\partial z'^2}. $$

A solution of the linearization of eq (6) can be found by assuming

$$\psi(r') = A \cos (q' \cdot r').$$

Given that \((\nabla^2 + q_0^2) \psi = (-q(t)^2 + q_0^2) \psi\) with \(q(t)^2 = q_{x'}^2 + (a(t)q_x' - q_z')^2\), we find

$$\frac{dA}{dt} = \epsilon A - (-q(t)^2 + q_0^2)^2 A = \sigma(t) A. $$

The disordered solution \(A = 0\) becomes unstable when

$$\int_0^{2\pi/\omega} \sigma(t') dt' > 0.$$ 

In analogy with the case analyzed in ref. [17], we find several instability modes and associated thresholds,

- \(q_x = 0, q_z = q_0\) \(\epsilon = 0\) parallel mode
- \(q_z = 0, q_x = \sqrt{\frac{4q_0^2 + 8}{3q_0^2 + 8q_0^2}} q_0\) \(\epsilon = \frac{\gamma q_0^4}{3q_0^2 + 8q_0^2 + 8}\) transverse mode
- \(q_x = \sqrt{\frac{2}{15\gamma^2 + 16}} q_0, \ q_z = \sqrt{\frac{3q_0^2 + 8}{15\gamma^2 + 16}} q_0\) \(\epsilon = \frac{8\gamma^2 q_0^4}{15\gamma^2 + 16}\) mixed mode

### 3 Envelope equation for a grain boundary under weak shear

We focus on a special configuration comprising two perfectly ordered lamellar domains, initially oriented perpendicular to each other that meet at a grain boundary. We assume that both domains are initially of same wavenumber \(q_0\) at least far from the boundary, so that a planar grain boundary would be stationary in the absence of shear. We will neglect in this study any back flow induced by the lamellae themselves (through osmotic stresses), so that the velocity field \(v\) in eq (5) equals the imposed shear flow. A schematic representation of the configuration under study is shown in Fig. 2. We denote by B the lamellae that lie parallel to the flow field, and note that the order parameter \(\psi\) in this region is unaffected by the flow. Transverse lamellae are denoted by A. If the A lamellae were to adiabatically follow the imposed flow, both orientation and wavelength would be a periodic function of time as illustrated schematically on Fig. 2. Because a local change in wavenumber away from \(q_0\) always leads to a free energy increase in region A, while the free energy in region B remains unchanged, we anticipate grain boundary motion from region B to region A, thereby increasing the area occupied by parallel lamellae.
We derive a set of amplitude equations from eq (8) by using a multiple scale approach. For \( \epsilon \ll 1 \), it is possible to extract the slow evolution of both the lamellae and the grain boundary (on a slow time scale \( \epsilon t \)) by expanding the order parameter \( \psi \) in both regions around a periodic function, with amplitudes that are slowly varying in the grain boundary region (of very large extent in this limit). Our derivation follows closely that of Tesauro and Cross for the case of no flow \cite{29}.

The analysis is restricted to shears of small amplitude and low frequency. Specifically, since \( -q(t)^2 + q_0^2 = -a^2 q_x^2 + 2ag_x q_y \), the shear contributes to eq (7) with two terms, one of order \( O(a^2) \) and the other of order \( O(a^4) \). Consistency with the expansion in the weak segregation limit requires that \( -q(t)^2 + q_0^2 \sim O(\epsilon) \), a requirement that dictates the magnitude of the shear amplitude. For the case considered below involving a grain boundary between parallel and transverse orientations, the cross derivative term \(-2ag_x q_y\) acting on the reference state vanishes, and therefore we will have \( -q(t)^2 + q_0^2 \sim O(a^4) \) or \( a \sim O(\epsilon^{1/4}) \).

We start by assuming that the slowly varying amplitude of mode \( e^{iq_0 x'} \) in region A has as characteristic length scales \( X = \epsilon^{1/2} x' \) and \( Z = \epsilon^{1/4} z' \), while the mode \( e^{iq_0 z'} \) in domain B has characteristic scales \( \bar{X} = \epsilon^{1/4} x' \) and \( \bar{Z} = \epsilon^{1/2} z' \). We further assume a weak shear so that \( a \sim \epsilon^{1/4} \). This scaling is appropriate for an initial configuration in which the transverse lamellae are parallel to the grain boundary (and therefore in the limit of small shear amplitude, the transverse lamellae will remain almost perpendicular to the parallel lamellae for all times). If the angle between the transverse lamellae and the grain boundary is finite, then the scaling \( a \sim \epsilon^{1/2} \) needs to be introduced instead. The operator \((\nabla^2 + q_0^2)^2\) can now be expanded in powers of \( \epsilon \) as

\[
(\nabla^2 + q_0^2)^2 = L_0^2 + \epsilon^{1/4}(2L_0 L_1) + \epsilon^{1/2}(L_1^2 + 2L_0 L_2) + \epsilon^{3/4}(2L_0 L_3 + 2L_1 L_2) + \epsilon(2L_0 L_4 + 2L_1 L_3 + L_2^2),
\]

where we have defined,

\[
L_0 = \partial_x^2 + \partial_x^2 + q_0^2
\]

\[
L_1 = 2(\partial_x \partial_X + \partial_x \partial_Z - a \partial_x \partial_Z)
\]

\[
L_2 = \partial_X^2 + \partial_Z^2 + 2(\partial_x \partial_X + \partial_x \partial_Z - a \partial_x \partial_X - a \partial_x \partial_Z) + a^2 \partial_x^2
\]

\[
L_3 = 2[\partial_X \partial_X + \partial_Z \partial_Z - a(\partial_x \partial_X + \partial_x \partial_Z + \partial_X \partial_Z) + a^2 \partial_x^2 \partial_X] \quad \text{and}
\]

\[
L_4 = \partial_X^2 + \partial_Z^2 - 2a(\partial_X \partial_Z + \partial_X \partial_Z) + a^2(2 \partial_x \partial_X + \partial_Z^2).
\]

We also expand \( \psi \) as

\[
\psi = \epsilon^{1/2} \psi_0 + \epsilon \psi_1 + \epsilon^{3/2} \psi_2 + ...
\]
and assume that both the frequency of the imposed shear, and the associated variation of \( \psi \) is over a slow time scale \( T = \epsilon t \). From eqs (6), (8) and (9) we obtain, at \( O(\epsilon^{1/2}) \) the equation

\[-L_0^2 \psi_0 = 0,\]

which admits the solution

\[\psi_0 = \frac{1}{\sqrt{3}}[A_0 e^{iq_0 x'} + B_0 e^{iq_0 z'} + c.c],\]

with \( A_0 \) and \( B_0 \) functions of \( X, Z, \bar{X}, \bar{Z} \) and \( T \). At \( O(\epsilon) \), eq (6) reduces to

\[-L_0^2 \psi_1 = L_1^2 \psi_0,\]

where we have used the fact that \( L_0 \psi_0 = 0 \), and taken advantage that the cross derivative term \( a\partial_x \partial_z \) vanishes when acting on \( \psi_0 \), so that the solution at this order is also time independent (in the sheared frame of reference). Since \( \psi_0 \) is an eigenmode of \( L_0 \) with zero eigenvalue, the right-hand side of eq (12) must vanish in order for it to admit a solution. Solvability requires that the scalar product

\[\langle \psi_0^+ | L_1^2 \psi_0 \rangle = 0,\]

that is, the right hand side of eq (12) is orthogonal to the the zero eigenfunctions of the adjoint of \( L_0 \). But

\[\langle \psi_0^+ | L_1^2 \psi_0 \rangle = \langle L_1^+ \psi_0^+ | L_1 \psi_0 \rangle = \| L_1 \psi_0 \|^2 = 0,\]

from which it follows \( L_1 \psi_0 = 0 \). As a result of this solvability condition, \( A_0 \) and \( B_0 \) must be independent of \( \bar{X} \) and \( Z \), respectively. Equation (12) then reduces to eq (10) and

\[\psi_1 = [A_1 e^{iq_0 x'} + B_1 e^{iq_0 z'} + c.c.] / \sqrt{3}.\]

Finally, at \( O(\epsilon^{3/2}) \), the multiple scale analysis yields the equation

\[L_0^2 \psi_2 = -\partial_T \psi_0 + \psi_0 - \psi_0^3 - (2L_0 L_1 + 2L_1 L_3 + L_2^2) \psi_0 - (2L_0 L_2 + L_2^2) \psi_1.\]

Again, the functions \( \psi_0 \) and \( \psi_1 \) are zero eigenmodes of the operator \( L_0 \), so that the projections of the terms in the right-hand side of eq (13) on these eigenfunctions must vanish. From this condition, we obtain the following amplitude equations

\[\partial_T A_0 = \{1 - [2iq_0(\partial_X - a\partial_Z) + \partial^2_z - q_0^2 a^2] \} A_0 - |A_0|^2 A_0 - 2|B_0|^2 A_0,\]

and,

\[\partial_T B_0 = \{1 - [2iq_0(\partial_Z - a\partial_X) + \partial^2_X] \} B_0 - |B_0|^2 B_0 - 2|A_0|^2 B_0,\]

where we have used the fact that \( L_0 \psi_0 = L_1 \psi_0 = 0 \) and have set \( L_1^2 \psi_1 = 0 \). This set of equations (14) and (15) governs the evolution of the slowly varying envelopes of the base lamellar pattern, including variations both in the direction parallel and perpendicular to the grain boundary. We now restrict our attention to the case of a planar grain boundary; hence we do not consider any dependence of the amplitudes on the coordinate parallel to the grain boundary. Transverse perturbations of the grain boundary are expected to decay back to planarity, and such decay will not
be considered here. Therefore \( A_0 \) and \( B_0 \) depend only on \( X \) and \( \bar{X} \) respectively. Equations (14) and (15) simplify to

\[
\partial_T A_0 = [1 - (2i q_0 \partial_X - q_0^2 a^2)^2] A_0 - |A_0|^2 A_0 - 2|B_0|^2 A_0, \tag{16}
\]

and,

\[
\partial_T B_0 = [1 - (\partial_X^2 - 2i a q_0 \partial_X)^2] B_0 - |B_0|^2 B_0 - 2|A_0|^2 B_0. \tag{17}
\]

In the absence of shear \((a = 0, x' = x)\), these two equations reduce to the case studied by Manneville and Pomeau [30], and by Tesauro and Cross [29].

Finally, we let \( \epsilon^{1/2} A_0 = r_A e^{i \phi_A} \), \( \epsilon^{1/2} B_0 = r_B e^{i \phi_B} \) where to lowest order \( \phi_A \) and \( \phi_B \) are independent of \( X \) and \( \bar{X} \) [31], and re-write the set of amplitude equations in the original (unscaled) set of variables. The resulting equations for \( r_A \) and \( r_B \) read

\[
\partial_t r_A = 4 q_0^2 \partial_X^2 r_A + (\epsilon - q_0^4 a^4) r_A - r_A^3 - 2 r_B^3 r_A, \tag{18}
\]

and,

\[
\partial_t r_B = -\partial_X^4 r_B + 4 a^2 q_0^2 \partial_X^2 r_B + \epsilon r_B - r_B^3 - 2 r_A^3 r_B. \tag{19}
\]

This is one of the main results of our calculation. At this order, there are two contributions to the amplitude equation arising from the shear. One in eq (18) which multiplies the second normal derivative of the amplitude \( r_B \). This contribution is nonzero only in the grain boundary region, of twice the frequency of the imposed shear, and describes variations of the amplitude of the parallel lamellae due to the changing orientation of the grain boundary with respect to the lamellar planes. As we will show below, this term alone originates an oscillatory contribution to the velocity of the grain boundary of zero average. The second contribution is the term \( q_0 a^4 r_A \) in eq (18). This term does not contain a spatial derivative, and therefore is important in the entire bulk region A where the amplitude \( r_A \) does not vanish. It leads to a change in the amplitude of the uniform transverse lamellae as they are advected by the flow. The corresponding change in the free energy of region A does not average to zero over a period and is responsible for the net motion of the grain boundary, as shown below.

The amplitude equations (18) and (19) need to be supplemented with appropriate boundary conditions. First we have that \( r_A(-\infty, t) = 0 \) and \( r_B(+\infty, t) = 0 \). Furthermore, at large distances from the grain boundary inside domain B, \( r_B \) reduces to the constant \( \sqrt{\gamma} \), independent of the flow parameters. By contrast, the amplitude \( r_A \) inside domain A satisfies the equation \( \partial_t r_A = (\epsilon - q_0^4 a^4) r_A - r_A^3 \) in the limit \( x' \to +\infty \). That equation admits the solution

\[
r_A(+\infty, t) = \{e^{-f(t)} [2 \int_0^t e^{f(t')} dt' + r_A^2 (+\infty, 0)]\}^{-1/2}, \tag{20}
\]

where \( f(t) = (2\epsilon - \frac{3}{4} q_0^4 a^4) t + q_0^4 a^4 \left( \frac{\sin 2\omega t}{2\omega} - \frac{\sin 4\omega t}{16\omega} \right) \). The asymptotic behavior of eq (20) at large times changes qualitatively with the sign of the constant \( 2\epsilon - \frac{3}{4} q_0^4 a^4 \).
When this constant is negative, the prefactor \( e^{-f(t)} \) diverges exponentially with time and \( r_A(+\infty, t) \) decays to zero. If, on the other hand, \( 2\epsilon - \frac{2}{3}q_0^4\gamma^4 > 0 \), Laplace’s method can be used to approximate the integral in the expression for \( r_A \), which reduces to a periodic function

\[
r_A(+\infty, t) = \left\{ \sqrt{\frac{\pi}{g(t)}} e^{h^2(t)/4g(t)} \text{erfc} \left[ \frac{h(t)}{2\sqrt{g(t)}} \right] \right\}^{-1/2}, \tag{21}
\]

where \( g(t) = \omega q_0^4 \gamma^4 (\sin 2\omega t - \frac{1}{2} \sin 4\omega t) \) and \( h(t) = 2\epsilon + q_0^4 \gamma^4 (\cos 2\omega t - \frac{1}{4} \cos 4\omega t - \frac{3}{4}) \). The condition \( 2\epsilon - \frac{3}{4}q_0^4\gamma^4 = 0 \) which separates these two cases can be understood in terms of a maximum strain amplitude \( \gamma^* = (8\epsilon/3q_0^4)^{1/4} \) above which the lamellar phase of domain A will melt. Note that \( \gamma^* \) is independent of the shear frequency \( \omega \).

We have numerically solved the coupled, one dimensional equations (18) and (19). The results that will be shown correspond to \( \epsilon = 0.04, q_0 = 1 \) and \( \gamma = 0.3 \), and a variety of shear frequencies. In the calculations, region A was surrounded by two identical domains of parallel (B) lamellae so that periodic boundary conditions in both directions could be used. The equations were integrated with a pseudo-spectral algorithm described in detail in ref. [17]. We used a computational domain of size \( L = 4096 \) and a grid spacing \( \Delta x = 0.5 \). The time interval \( \Delta t \) was chosen as a function of the period of the shear as \( \Delta t = 2\pi/(50000\omega) \). Stationary solutions obtained in the absence of shear provided the initial conditions for \( r_A \) and \( r_B \).

The instantaneous location of the grain boundary \( x^* \) was defined as \( r_B(x^*) = \sqrt{\epsilon}/2 \), and its velocity \( v_{gb} \) as the rate of change of \( x^* \). Figure 3 shows \( v_{gb} \) as a function of time for several values of the angular frequency \( \omega \). Time has been scaled by the period \( \tau = 2\pi/\omega \) of the applied shear. Positive (resp. negative) values of \( v_{gb} \) indicate motion toward lamellae in domain A (resp. B). Following an initial transient, the velocity oscillates in time at half the period of the shear, with an amplitude that decreases with the frequency. Note also that the average velocity is positive; i.e., motion is directed toward domain A. It is possible to further interpret these results by obtaining an analytic approximation for the boundary velocity in the limit of very low frequencies. If the frequency is sufficiently low, the order parameter \( \psi \) (or the amplitudes \( r_A \) and \( r_B \)) will adiabatically follow the motion of the boundary. In this limit it is possible to invoke a quasi-static approximation according to which \( r_A(x', t) \simeq r^*_A(x' - x'_{gb}(t); a) \) and \( r_B(x', t) \simeq r^*_B(x' - x'_{gb}(t); a) \), where \( r^*_A \) and \( r^*_B \) are stationary solutions of eqs (18) and (19) (with the boundary conditions given, including eq (21)) that still formally depend on the parameter \( a \). This latter dependence results from the dependence of the stationary amplitude profiles \( r^*_A \) and \( r^*_B \) on the state of shear of the system given by the parameter \( a \). Then \( (\partial_1 r_A, \partial_1 r_B) \simeq -v_{gb} (\partial_2 r^*_A, \partial_2 r^*_B) \) where we have introduced the notation \( \bar{x} = x' - x'_{gb} \). Following Manneville and Pomeau [30], we multiply eq (18)
by $\partial z r^A_\lambda$ and eq \[(19)\] by $\partial z r^B_\lambda$, add the two equations and integrate over $\tilde{x}$ to obtain

$$-v_{gb} \int_{-\infty}^{+\infty} d\tilde{x} \left[ (\partial z r^A_\lambda)^2 + (\partial z r^B_\lambda)^2 \right] = K(+\infty) - K(-\infty), \tag{22}$$

where

$$K(\tilde{x}) = \frac{1}{2} \left\{ (\epsilon - q_0^4 a_4^4) r^A_\lambda^2 + \epsilon r^B_\lambda^2 - \frac{1}{2}(r^A_\lambda^4 + r^B_\lambda^4) - 2r^A_\lambda^2 r^B_\lambda^2 + 4q_0^3 (\partial z r^A_\lambda)^2 + 4a^2 q_0^2 (\partial z r^B_\lambda)^2 - 2 \left( (\partial^2 z r^A_\lambda)(\partial z r^B_\lambda) - \frac{1}{2}(\partial^2 z r^B_\lambda)^2 \right) \right\}.$$

The integral in the left-hand side of eq \[(22)\] is an inverse mobility or friction coefficient, whereas the right-hand side is the effective driving force for grain boundary motion. It is equal to the static free energy increase of the configuration upon shearing relative to the planar, unshared boundary and can be evaluated by using the values $r^A_\lambda(-\infty) = 0, r^A_\lambda(+\infty) = \sqrt{\epsilon}$ and $r^B_\lambda(+\infty) = 0$. Furthermore in the quasistatic limit the function $g(t)$ appearing in eq \[(21)\] is small, and $r^A_\lambda \approx \sqrt{\epsilon - q_0^4 a_4^4}$. As a result, $K(-\infty) = \epsilon^2/4, K(+\infty) = (\epsilon - q_0^4 a_4^4)/4$ and

$$v_{gb} = \frac{q_0^4 \gamma^4 \sin^4(\omega t)[2\epsilon - q_0^4 \gamma^4 \sin^4(\omega t)]}{4 \int_{-\infty}^{+\infty} d\tilde{x} \left[ (\partial z r^A_\lambda)^2 + (\partial z r^B_\lambda)^2 \right]}.$$

We now compare this result with those obtained by numerical integration of the governing equations and shown in Fig. 3 for a range of angular frequencies. In order to compute the inverse mobility coefficient that appears in the denominator of eq \[(23)\], we have obtained $r_A(x', t)$ and $r_B(x', t)$ directly by integration of eqs \[(18)\] and \[(19)\]. Equation \[(23)\] agrees very well with the numerical value of $v_{gb}$ at very small shear frequencies, as illustrated in Figure 3 for $\omega = 0.001$. The agreement progressively deteriorates as the angular frequency increases.

We finally note that although the time dependence of $v_{gb}$ changes significantly with $\omega$, its average over a period $\langle v_{gb} \rangle = (1/\tau) \int_0^\tau v(t) \, dt$ only shows a weak dependence on shear frequency, as shown in figure 4. We find, for example, that increasing the shear frequency by two orders of magnitude causes a decrease of only 5% in the average speed of the grain boundary. This result follows from the fact that the effective driving force $K(-\infty) - K(+\infty)$ responsible for the motion of the grain boundary is independent of the shear frequency in the quasistatic limit and increases only marginally at larger frequencies. As a result, variations in velocity with $\omega$ arise solely from the small changes of the inverse mobility coefficient on frequency. Somewhat unexpectedly, the quasistatic approximation does quite well at predicting the average velocity of the grain boundary for a wide range of frequencies. We show in Fig. 4 $\langle v_{gb} \rangle$ obtained by averaging both sides of eq \[(22)\] over a period, and the numerical results of Fig. 3 also averaged over a period of the shear.
4 Discussion

Following a quench of the diblock copolymer from an initially disordered configuration at $T > T_{ODT}$ to a final temperature below $T_{ODT}$, the following qualitative picture emerges concerning the asymptotic, long time selection of a lamellar orientation relative to the shear. In the absence of shear ($\gamma = 0$), initial composition fluctuations are amplified exponentially, with a growth rate that is isotropic. Lamellar regions emerge and coarsen as a function of time. Coarsening rates and the role of topological defects in a two dimensional system have been discussed in ref. [32]. To our knowledge, a similar investigation in three dimensions has not been carried out. If the quench takes place under shear, the mean field instability threshold depends on orientation, as shown in ref. [17]. The first threshold is to a mixed parallel-perpendicular mode at $B_c = 1/4$, followed by a bifurcation to a transverse mode at $B_c = 1/4 - \gamma^4/32 + O(\gamma^6)$, and to a parallel-transverse mode at $B_c = 1/4 - \gamma^2/8 + O(\gamma^4)$. Therefore for shallow quenches fluctuations along different orientations would be amplified at different rates leading to predominantly parallel and perpendicular oriented domains even from an isotropic initial condition. Thermal fluctuations, on the other hand, are known to significantly modify these conclusions [25, 33, 26, 34]. In particular, thermal fluctuations render the mean field supercritical bifurcation a weakly subcritical bifurcation, with a transition temperature that increases with $\gamma$. In any event, the distribution of orientations following a quench in shear flow is expected not to be isotropic.

Regardless of whether the copolymer is quenched in shear flow or not, a macroscopically disordered configuration will result at intermediate times comprising regions of well saturated monomer composition, but with a wide distribution of lamellar orientations. The distribution of observable orientations is reduced by the shear, as those orientations that are unstable against long wavelength perturbations will quickly decay when the monomer composition locally reaches nonlinear saturation. Insofar the melt is Newtonian at the low shear frequencies investigated in refs. [17, 18], one would expect lamellae that are predominantly perpendicular, and to a lesser degree parallel, with small projections of the lamellar wavevector on the transverse direction. There also exists a small region of stable transverse lamellae. Further structure coarsening under shear will involve an initially anisotropic distribution of orientations, and hence is expected to be qualitatively different from the isotropic case. In metals, for example, coarsening of an initially anisotropic distribution of orientations leads to texture [35].

The results of this paper further indicate that regions where parallel and transverse lamellae meet will move, even when both parallel and transverse lamellae are linearly stable. The net motion of the grain boundary is driven by free energy reduction because parallel lamellae are unaffected by the shear, whereas transverse lamellae are elastically compressed, a compression that leads to an increase in energy that is relieved through boundary motion. Since a similar argument can be
made for a boundary separating perpendicular and transverse lamellae, we would ex-
pect that regions of a macroscopic sample oriented along any combination of parallel 
and perpendicular orientations will grow at the expense of any remaining transverse 
lamellae.

We are then confronted with an interesting question concerning the behavior of 
boundaries separating parallel and perpendicular lamellae. Both orientations show 
fluid like response to the shear, in contrast with the (one dimensional) elastic response 
of the transverse orientation. In fact, the flow does not couple to the monomer 
composition for the simple model of Newtonian melt with constant viscosity adopted 
here, and hence there are no shear flow effects on this type of boundary.

If viscous or viscoelastic contrast between the microphases is allowed, a secondary 
flow appears which is orientation dependent. The velocity field of this secondary 
flow is parallel to the lamellar planes (assuming incompressibility), and largest 
for a uniform parallel configuration, while it vanishes for a uniform perpendicular 
configuration. This flow is weak in the weak segregation limit, and has negligible 
consequences on the stability of a lamellar configuration against long wavelength 
perturbations. However, its possible effect on boundary motion has not been 
investigated yet. For long wavelength modulations of the type described by ampli-
tude equations, it is possible that the effect of these secondary flows can be subsumed 
into an effective constitutive relation for the dissipative part of the stress tensor as a 
function of the velocity gradient tensor. This constitutive relation has to be compat-
ible with the uniaxial symmetry of a lamellar phase, in analogy with other uniaxial 
systems such as nematic or smectic liquid crystals. Additional viscosity coefficients 
would enter the constitutive law, as well as an explicit dependence on $q$, the slowly 
varying normal to the lamellar planes. In this case, the effective viscosity of a region 
of parallel lamellae is different from that of perpendicular lamellae thus leading to 
secondary flows that are asymmetric with respect to the boundary, and possibly to 
boundary motion. This possibility is currently under investigation.

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FIGURE CAPTIONS

Figure 1. Schematic representation of the geometry considered including the shear direction, and the three different lamellar orientations discussed in the text.

Figure 2. Schematic representation of a planar grain boundary that separates regions of parallel and transverse lamellae being uniformly sheared.

Figure 3. Grain boundary velocity as a function of time obtained by numerical solution of eqs (14) and (15). Four different angular frequencies are shown: (in order of decreasing amplitude) $\omega = 0.001, 0.01, 0.05, \text{ and } 0.1$. Also shown is the quasistatic approximation of eq (23) calculated at the lowest angular frequency $\omega = 0.001$. The curve is indistinguishable in the graph from the corresponding numerical solution.

Figure 4. Temporal average of the grain boundary velocity as a function of the angular frequency of the shear. The symbols correspond to the time average of the numerically obtained velocities shown in Fig. 3, and the solid line is the time average of the quasistatic velocity given in eq (23).
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