Anisotropic linear response in block copolymer lamellar phases

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Abstract

We examine the linear response of a lamellar block copolymer phase in the weak segregation regime, and focus on those effects that arise from the uniaxial symmetry of the phase. The classical two fluid model of a polymer solution is extended to allow for anisotropic monomer diffusion as well as hydrodynamic flows. The latter include constitutive laws for the stress that also reflect the symmetry of the phase. Transverse relaxation of weakly perturbed lamellae is the slowest mode, and is sub-diffusive, in contrast to diffusive decay of longitudinal perturbations. Anisotropic diffusion can both enhance or reduce the rate of relaxation of long wavelength perturbations of lamellae depending on the relative magnitude of longitudinal and transverse mobilities. Hydrodynamic flows at the scale of the lamellae are negligible for most situations of interest, but not long ranged flows as would appear in, for example, multi domain configurations. We find that such flows accelerate linear decay, and even dominate diffusive relaxation in the long wavelength limit. We finally examine anisotropic effects on defect motion as exemplified by a tilt grain boundary. The boundary velocity is significantly affected by anisotropic diffusion through the coupling between undulation and permeation diffusive modes in the defect region.

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Introduction

Block copolymers are finding numerous applications in nanotechnology,[1,2] and have been of great interest in soft matter science because of the properties that derive from their microphase separation to ordered phases of a wide variety of symmetries (for a brief review see Ref. 3 and references therein). Microphase separation also brings about interesting dynamical properties, including unusual rheological response[4–8] and orientation selection during shear aligning.[9,10] We describe here a long wavelength and low frequency order parameter model that is consistent with the uniaxial symmetry of a lamellar phase, and explore some the consequences for the relaxation of weakly perturbed lamellar phases and motion of defects.

Order parameter models that describe the equilibrium properties and phase diagram of diblock copolymers were given in Refs. 11–14. In addition, the so called two fluid model has been widely used to describe the dynamical behavior of polymer solutions and blends in the low frequency hydrodynamic regime (compared with inverse relaxation times of the polymer chains) and long wavelength (compared with their radius of gyration).[15–17] More recently, the two fluid model has been further extended to describe the dynamics of block copolymer melts, including a quantitative description of the microscopic details of the polymer chain through Self Consistent Field Theory.[18,19] The resulting governing equations include dissipative dynamics for the order parameter driven by free energy reduction from a functional obtained through Self Consistent Field Theory, and over damped (or Stokesian) dynamics for hydrodynamic flows. However, both dissipative relaxation of the order parameter and momentum transport equations assume that the block copolymer phase is isotropic. We wish to investigate here some of the limitations of this assumption.

In principle, the low frequency and long wavelength hydrodynamic equations of motion for ordered systems can be derived by considering conservation laws and symmetry arguments.[20,21] For a diblock copolymer there are six conservation laws: total number of each monomer, three components of momentum, and energy. In addition, when a diblock copolymer undergoes an order-disorder transition to a lamellar phase, a new hydrodynamic variable arises associated with the broken translational symmetry of a lamellar phase (smectic symmetry). We restrict our attention

to an isothermal sample, and assume that the melt is incompressible. With this assumption the total number and energy conservation laws drop out. It is then sufficient to consider a description based on a periodic order parameter ψ in which amplitude and phase of describe local changes of composition and distortions of the layers respectively, and a velocity field $\mathbf{v}$. By employing the conventional method described in Refs.20,21 one can derive the hydrodynamic equations for ψ and $\mathbf{v}$ that reflect the uniaxial symmetry of a lamellar phase.[22,23] Unlike earlier research[18,19] in which the melt was assumed to be isotropic, the resulting equations of motion involve an anisotropic mobility tensor and a constitutive relation for the dissipative stress with three viscosity coefficients.

Previous studies of the effects of hydrodynamic flows on the dynamics of composition fluctuations include an analysis of the high temperature, homogeneous phase of diblock copolymers,[24] flows in polymer solutions,[25] the isotropic-to-lamellar transition of polymer solutions[26,27] and a study of hydrodynamic effects in layered phases.[28] The stationary structure factor under steady shear flow has been computed to show that order parameter fluctuations are greatly affected by the flow. In particular, shear flow distorts the director away from the layer normal in Smectic A liquid crystals in such a way that the undulation mode (associated with the rippling of the layers) becomes an "elastic" mode.[28]

We do not consider here a steady external shear. Instead, flows are driven by lamellar distortion. This internally generated flows produce similar effects to those in Smectic A liquid crystals: For small wavevector perturbations perpendicular to the lamellar normal hydrodynamic flows couple only with the phase of order parameter, and can dominate the relaxation process for sufficiently long wavelenghts. No hydrodynamic effects appear for perturbations parallel to the layer normal (permeation mode).

This paper is organized as follows. In section 2 we present the hydrodynamic equations of motion for diblock copolymers in a lamellar phase. This requires both an anisotropic mobility tensor for order parameter diffusion, and anisotropic viscosities for the dissipative stress tensor. Next, we investigate the effect of hydrodynamic flow and anisotropic diffusion on linear relaxation of lamellae subject to weak distortions parallel and perpendicular to layers in section 3, and the

motion of a tilt grain boundary in section 4.

Model equations

The equations governing the dynamics of an AB diblock copolymer in its lamellar phase can be derived by using conservation laws and broken symmetry arguments.[20,21,23] According to the two-fluid model for polymer solutions, blends, or diblock copolymers[15–17] one introduces two continuity equations for each monomer

$$\partial_t \rho_A = -\partial_i(\rho_A v_{iA}), \tag{1}$$

$$\partial_t \rho_B = -\partial_i(\rho_B v_{iB}), \tag{2}$$

where $\rho_{A,B}$ and $v_{iA,B}$ are the monomer number fraction and the corresponding velocities with A and B denoting polymers and solvent for polymer solutions, or two types of monomers in polymer blends or diblock copolymers. It is customary to introduce an order parameter $\psi = \rho_A - \rho_B$ so that

$$\partial_t \psi + \partial_i J_i = 0, \tag{3}$$

where the flux J_i has both a reversible part J_i^R that accounts for advection of ψ, and a dissipative part J_i^D responsible for energy dissipated due to the relative motion of the two types of monomers. By taking the difference of the continuity equations, the order parameter equation Eq. (3) contains a reversible current $J_i^R = \psi v_i$ where the average flow velocity is $v_i = \rho_A v_{iA} + \rho_B v_{iB}$ with $\rho_A + \rho_B = 1$, and a dissipative current

$$J_i^D = 2\rho_A \rho_B \left[v_{iA} - v_{iB} \right]. \tag{4}$$

According to the two-fluid model, the relative velocity between two monomers in J_i^D is obtained by employing a Rayleigh's variational principle[29] in which a dissipation function is introduced that contains the square of the relative velocity times an isotropic friction coefficient γ. Under this

assumption, the resulting dissipative current is[15–19]

$$J_i^D = -\gamma^{-1}(\rho_A \rho_B)^2 \partial_i \mu, \tag{5}$$

where $\mu = \mu_A - \mu_B$ is the difference in the monomer chemical potentials.

The constitutive law Eq. (5), however, must reflect the symmetry of the ordered phase. In general, one writes

$$J_i^D = -\Lambda_{ij} \partial_j \mu, \tag{6}$$

with Λ_{ij} a kinetic mobility tensor. The number of independent components of Λ_{ij} is determined by the symmetry of the phase. For layered systems of uniaxial symmetry, there are only two independent components: A longitudinal part Λ_L and a transverse part Λ_T,

$$\Lambda_{ij} = \Lambda_L n_i n_j + \Lambda_T (\delta_{ij} - n_i n_j), \tag{7}$$

where n_i is the unit normal to the lamellar layers. Alternatively, the kinetic mobility tensor can be decomposed into a scalar (isotropic) part Λ_I and a traceless (anisotropic) part Λ_A:

$$\Lambda_{ij} = \Lambda_I \delta_{ij} + \Lambda_A \left(n_i n_j - \frac{1}{3} \delta_{ij} \right), \tag{8}$$

where $\Lambda_I = \Lambda_L/3 + 2\Lambda_T/3$ and $\Lambda_A = \Lambda_L - \Lambda_T$. We will use both sets of mobilities in subsequent calculations. In the hydrodynamic limit when lamellae are weakly perturbed, the unit vector n_i varies slowly. We assume that in this limit Λ_{ij} retains the same functional form with the local principal axis defining the local normal to the perturbed layers.

For lamellar diblock copolymers in the weak segregation limit the relative chemical potential is obtained by taking the functional derivative with respect to ψ of the free energy functional given by[11–13]

$$F = \frac{1}{2} \int d^3x \left\{ -r\psi^2 + \frac{u}{2}\psi^4 + \xi \left[(\nabla^2 + q_0^2)\psi \right]^2 \right\}, \tag{9}$$

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where q_0 is the wavenumber of the layers, and r, u, and ξ are coefficients that depend on the material properties of the block copolymer. Since the reversible current $J_i^R = \psi v_i$, and with Eq. (6) for J_i^D, the order parameter equation Eq. (3) becomes

$$\partial_t \psi + \partial_i (\psi v_i) = \partial_i \left[\Lambda_{ij} \partial_j \left(\frac{\delta F}{\delta \psi} \right) \right]. \tag{10}$$

The coupling term to flow velocity describes advection of order parameter whereas the right hand side reflects anisotropic diffusion of order parameter.

Given the high viscosity of block copolymer melts, the momentum conservation equation is considered in the over damped limit (small Reynold number)

$$\partial_i P - \partial_j \sigma_{ij}^R - \partial_j \sigma_{ij}^D = 0, \tag{11}$$

which has an implicit dependence on velocity. In this equation P is the hydrostatic pressure, σ_{ij}^R is the reversible elastic stress tensor, and σ_{ij}^D is the dissipative stress tensor. The gradient of the reversible elastic stress tensor is simply[23,30,31]

$$\partial_j \sigma_{ij}^R = -\psi \partial_i \left(\frac{\delta F}{\delta \psi} \right). \tag{12}$$

Since there is no external stress to generate hydrodynamic flows, the flow velocity $\mathbf{v}$ is produced only by fluctuations in ψ as given by the so called osmotic stress tensor in Eq. (12). For linearly stable lamellae, excess reversible stresses due to distortion of the morphology will be dissipated in part through hydrodynamic flow.

For fluids of uniaxial symmetry there are five independent viscosities in σ_{ij}^D,[32] although the number reduces to three under the assumption of incompressibility. The dissipative stress tensor can be written as[32]

$$\sigma_{ij}^D = \alpha_1 n_i n_j n_k n_l v_{kl} + \alpha_4 v_{ij} + \alpha_{56} n_k (n_i v_{kj} + n_j v_{ki}), \tag{13}$$

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where the strain rate tensor is $v_{ij} = (\partial_i v_j + \partial_j v_i)/2$, and α_1, α_4 and α_{56} are three constant viscosities. Within the order parameter model description, we assume that for slow spatial variations in the lamellar order, Eq. (13) holds locally.

In summary, Eq. (7), Eq. (10), and Eq. (13) plus the incompressibility condition $\partial_i v_i = 0$ are the governing equations for the evolution a lamellar phase in a diblock copolymer. Before we proceed any further, we recast the governing equations of motion in terms of dimensionless quantities: $\mathbf{x}' = q_0\mathbf{x}$, $t' = \xi\Lambda_I q_0^6 t$, $\psi' = \psi/\sqrt{\xi/u}q_0^2$, and $F' = F/(\xi^2 q_0^5/u)$. With the newly defined variables the order parameter equation can be rewritten as

$$\partial_t \psi + v_i \partial_i \psi = \partial_i \left[\Lambda_{ij} \partial_j \left(\frac{\delta F}{\delta \psi} \right) \right], \tag{14}$$

with the free energy being

$$F = \frac{1}{2} \int d^3x \left\{ -\varepsilon \psi^2 + \frac{1}{2}\psi^4 + \left[(\nabla^2 + q_0^2)\psi \right]^2 \right\}, \tag{15}$$

and the anisotropic kinetic tensor

$$\Lambda_{ij} = \bar{\Lambda}_L n_i n_j + \bar{\Lambda}_T (\delta_{ij} - n_i n_j), \tag{16}$$

or

$$\Lambda_{ij} = \delta_{ij} + \Lambda \left(n_i n_j - \frac{1}{3}\delta_{ij} \right), \tag{17}$$

where $\varepsilon = r/\xi q_0^4 \ll 1$, $\bar{\Lambda}_L = \Lambda_L/\Lambda_I$, $\bar{\Lambda}_T = \Lambda_T/\Lambda_I$, and $\Lambda = \Lambda_A/\Lambda_I$. The positiveness of $\bar{\Lambda}_L$ and $\bar{\Lambda}_T$ lead to $-3/2 < \Lambda < 3$. In addition, the momentum conservation equation becomes

$$\partial_i P + \zeta \psi \partial_i \left(\frac{\delta F}{\delta \psi} \right) - \partial_j \sigma_{ij}^{\mathrm{D}} = 0, \tag{18}$$

where we have used the viscosity α_4 to rescale the dissipative stress tensor such that

$$\sigma_{ij}^{\mathrm{D}} = \alpha_1 n_i n_j n_k n_l v_{kl} + v_{ij} + \alpha_{56} n_k (n_i v_{kj} + n_j v_{ki}). \tag{19}$$

In the rescaled momentum conservation equation, the hydrodynamic coupling coefficient $\zeta = \xi q_0^2 / \Lambda_I u \alpha_4$ plays the role of an inverse capillary number.[31] The reader should also note that we have omitted the primes and, for clarity, retained $q_0 = \|\mathbf{q}_0\| = 1$ explicitly.

Relaxation of Diblock Copolymer Lamellae

We begin by investigating the linear relaxation of weakly perturbed lamellae to obtain the relaxation time scales as a function of the strength of the anisotropy and of hydrodynamic coupling. Consider as reference state a stationary solution of the order parameter Eq. (14) describing an ordered lamellar phase,

$$\psi_s(\mathbf{r}) = \psi_1 \cos(\mathbf{q} \cdot \mathbf{r}). \tag{20}$$

where $\mathbf{q}$ is the wave vector of the reference state. We introduce a small disturbance of wave number $Q \ll q$ such that

$$\psi(\mathbf{r},t) = \psi_1 \cos(\mathbf{q} \cdot \mathbf{r}) + \psi_2(t) \exp[i(\mathbf{q} + \mathbf{Q}) \cdot \mathbf{r}]$$
$$+ \psi_3(t) \exp[i(\mathbf{q} - \mathbf{Q}) \cdot \mathbf{r}] + \text{c.c.} + \dots, \tag{21}$$

where c.c. stands for complex conjugation. The time dependent amplitudes $\psi_2(t)$, $\psi_3(t)$ and their complex conjugates are assumed to be small compared to the amplitude ψ_1 of the reference state.

Since we are interested in linear response, the local unit normal to perturbed lamellae is simply the wavevector of the reference state, $n_i \simeq q_i/q$, thus neglecting its fluctuations. The kinetic tensor, Eq. (16), becomes uniform, and only depends on the reference state

$$\Lambda_{ij} = \bar{\Lambda}_L \frac{q_i q_j}{q^2} + \bar{\Lambda}_T \left(\delta_{ij} - \frac{q_i q_j}{q^2} \right), \tag{22}$$

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from which the order parameter equation, Eq. (14), reduces to

$$\partial_t \psi + v_i \partial_i \psi = \Lambda_{ij} \partial_i \partial_j \left(\frac{\delta F}{\delta \psi} \right) \tag{23}$$

where

$$\frac{\delta F}{\delta \psi} = -\varepsilon \psi + \psi^3 + (\nabla^2 + q_0^2)^2 \psi. \tag{24}$$

We follow Zhang's study in Ref. 23 on the effect of hydrodynamic flows on the relaxation of lamellar block copolymers to derive the amplitude equations by replacing Eq. (21) into Eq. (23). In deriving the amplitude equations, we retain only terms linear in $\psi_{2,3}(t)$ and $\psi_{2,3}^*(t)$, and of six relevant modes, $\pm\mathbf{q}$ and $\pm(\mathbf{q} \pm \mathbf{Q})$, and omit higher order modes that arise from mode coupling terms in Eq. (23). We focus on the linear stability of two different modes: a permeation (longitudinal) mode, $\mathbf{Q} \parallel \mathbf{q}$, and an undulation (transverse) mode, $\mathbf{Q} \perp \mathbf{q}$.

We start by analyzing the anisotropic diffusion term in Eq. (23). By substituting the perturbed order parameter Eq. (21) into Eq. (23), the excess of free energy due to the perturbation Eq. (24) becomes [in Fourier space $(\mathbf{k}, \omega)$],

$$\begin{aligned} \left[\frac{\delta F}{\delta \psi} \right] (\mathbf{k}, \omega) &= (2\pi)^4 M_0 \frac{\psi_1}{2} \delta(\omega) \delta(\mathbf{k} + \mathbf{q}) + (2\pi)^4 M_0 \frac{\psi_1}{2} \delta(\omega) \delta(\mathbf{k} - \mathbf{q}) \\ &+ (2\pi)^3 \Big[M_1(\omega) \delta(\mathbf{k} - \mathbf{q} - \mathbf{Q}) + M_1^*(\omega) \delta(\mathbf{k} + \mathbf{q} + \mathbf{Q}) \\ &+ M_2(\omega) \delta(\mathbf{k} - \mathbf{q} + \mathbf{Q}) + M_2^*(\omega) \delta(\mathbf{k} + \mathbf{q} - \mathbf{Q}) \Big], \end{aligned} \tag{25}$$

where

$$M_0 = -\varepsilon + (q^2 - q_0^2)^2 + \frac{3}{4}\psi_1^2, \tag{26}$$

$$M_1(\omega) = -\varepsilon \psi_2(\omega) + \left[|\mathbf{q} + \mathbf{Q}|^2 - q_0^2 \right]^2 \psi_2(\omega) + \frac{3}{4}\psi_1^2 \left[2\psi_2(\omega) + \psi_3^*(\omega) \right], \tag{27}$$

$$M_2(\omega) = -\varepsilon \psi_3(\omega) + \left[|\mathbf{q} - \mathbf{Q}|^2 - q_0^2 \right]^2 \psi_3(\omega) + \frac{3}{4}\psi_1^2 \left[2\psi_3(\omega) + \psi_2^*(\omega) \right], \tag{28}$$

where $\psi_{2,3}^*(\omega)$ are the temporal Fourier transforms of the complex conjugates of $\psi_{2,3}(t)$, respec-

tively. With Eq. (25) the right hand side of Eq. (23) becomes

$$
\begin{aligned}
-\Lambda_{ij}k_ik_j\left[\frac{\delta F}{\delta \psi}\right](\mathbf{k},\omega) &= -\Lambda_{ij}q_iq_j(2\pi)^4 M_0\frac{\psi_1}{2}\delta(\mathbf{k}+-\mathbf{q})\delta(\omega) \\
&\quad -\Lambda_{ij}(q_i+Q_i)(q_j+Q_j)(2\pi)^3 M_1(\omega)\delta(-\mathbf{k}-\mathbf{q}-\mathbf{Q}) \qquad (29) \\
&\quad -\Lambda_{ij}(q_i-Q_i)(q_j-Q_j)(2\pi)^3 M_2(\omega)\delta(-\mathbf{k}-\mathbf{q}+\mathbf{Q})+\text{c.c}
\end{aligned}
$$

where in complex conjugation (c.c.) a sign change of mode is implied, e.g., $\delta(\mathbf{k}-\mathbf{q}-\mathbf{Q}) \to \delta(\mathbf{k}+\mathbf{q}+\mathbf{Q})$.

Next, we turn our attention to the advection term in Eq. (23). For the permeation mode ($\mathbf{Q} \parallel \mathbf{q}$) the direction of the gradient of the order parameter coincides with the normal direction to the layers ($\mathbf{k} \parallel \mathbf{n}$), whereas the direction of the velocity should be perpendicular to the unit normal $\mathbf{n}$ because of the incompressibility condition. As a consequence, the advection term ($v_i\partial_i\psi_s \sim v_in_i$) vanishes, and there is no hydrodynamic flow corresponding to the permeation mode.

For the undulation mode [$\mathbf{Q} \perp \mathbf{q}(\sim \mathbf{n})$], the direction of the gradient of order parameter is perpendicular to the unit normal $\mathbf{n}$, which implies that $n_ik_i = 0$, and the velocity becomes parallel to $\mathbf{n}$ because of the incompressibility condition. Therefore, the advection term does not vanish. In the linear regime, the velocity field couples only to the gradient of reference state ψ_s, and the advection term reduces to

$$
\begin{aligned}
\left[v_i\partial_i\psi\right](\mathbf{k},\omega) &= \int\frac{d^3k_1 d\omega_1}{(2\pi)^4}v_i(\mathbf{k}-\mathbf{k}_1,\omega-\omega_1)ik_{1i}\psi(\mathbf{k}_1,\omega_1) \\
&= -iq_i\frac{\psi_1}{2}\left[v_i(\mathbf{k}+\mathbf{q})-v_i(\mathbf{k}-\mathbf{q})\right].
\end{aligned} \qquad (30)
$$

Since the relevant modes in the order parameter equation are $\mathbf{k} = \pm(\mathbf{q}\pm\mathbf{Q})$, the relevant velocity modes which couple to the reference state should be of the perturbing wavenumber $\pm\mathbf{Q}$.

We now use the momentum conservation equation to write the velocity in terms of ψ. First, we take the gradient of the momentum conservation equation Eq. (18), and solve for the pressure in Fourier space. Next, the obtained pressure is substituted back into the momentum conservation

equation, resulting in

$$v_i(\mathbf{k},\omega) = -\frac{2\zeta}{1+\alpha_{56}}\frac{1}{k^2}\left(\delta_{ij} - \frac{k_i k_j}{k^2}\right) f_j(\mathbf{k},\omega),$$ (31)

where the reversible force associated with the order parameter perturbation is given by $f_i = \psi_s \partial_j (\delta F / \delta \psi)$. In obtaining Eq. (31) we have used the fact that, in the linear regime, the velocity must be linear in the perturbation amplitudes. It is also worth mentioning here that the velocity v_i does not depend on the viscosity coefficient α_1 because we are considering an undulation mode in an incompressible fluid.

Similar to the case of advection term, we find from Eq. (31) that the free energy change of modes $\pm(\mathbf{q}\pm\mathbf{Q})$ couples to the reference state because the relevant modes of the flow velocity are $\pm\mathbf{Q}$. Therefore, the first two terms in the right hand side of Eq. (25) can be neglected, and we now obtain the velocity in terms of the amplitudes of the perturbation by substituting Eq. (21) and Eq. (25) into Eq. (31),

$$\begin{aligned}v_i(\mathbf{k},\omega) = &-i(2\pi)^3\frac{2\zeta}{1+\alpha_{56}}\frac{\psi_1}{2}\frac{q_j}{k^2}\left(\delta_{ij} - \frac{k_i k_j}{k^2}\right)\delta(\mathbf{k}+\mathbf{Q})\times \\ &\times \left[M_2(\omega) - M_1^*(\omega) + \psi_2^*(\omega)M_0 - \psi_3(\omega)M_0\right] + \text{c.c},\end{aligned}$$ (32)

The resulting advection term in the order parameter equation is,

$$\begin{aligned}\left[v_i\partial_i\psi\right](\mathbf{k},\omega) = &H_\perp \delta(\mathbf{k}-\mathbf{q}-\mathbf{Q})\left[M_1(\omega) - M_2^*(\omega) - \psi_2(\omega)M_0 + \psi_3^*(\omega)M_0\right] \\ &+ H_\perp \delta(\mathbf{k}-\mathbf{q}+\mathbf{Q})\left[M_2(\omega) - M_1^*(\omega) - \psi_3(\omega)M_0 + \psi_2^*(\omega)M_0\right] + \text{c.c}\end{aligned}$$ (33)

where we have introduced a wavenumber dependent hydrodynamic coupling coefficient

$$H_\perp = \frac{2}{3}\frac{\zeta}{1+\alpha_{56}}\frac{q^2}{Q^2}\left[\varepsilon - (q^2 - q_0^2)^2\right],$$ (34)

which is what one would obtain if an effective *isotropic* dissipative stress tensor with shear viscosity $\alpha_4 + \alpha_{56}$ is considered.

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The hydrodynamic coupling coefficient has an explicit dependence proportional to $1/Q^2$ arising from viscous damping of the induced velocity modes of wavenumber $\pm\mathbf{Q}$. The advection scale contains this scaling of the hydrodynamic coupling and that of the amplitudes M_i [Eq. (26) - Eq. (28)]. We now show that the combination of the two leads to a decay rate of the phase of order parameter proportional to Q^2 rather than the expected decay rate $\sim Q^4$ in uniaxial systems.[33]

By combining the self-diffusion term Eq. (25) and the hydrodynamic term Eq. (33) we can write the amplitude equations in a general form. We present them separately for different modes in the small $\mathbf{Q}$ limit. First there is an equation corresponding to modes $\pm\mathbf{Q}$ which defines the amplitude of the reference wave ψ_1

$$\psi_1^2 = \frac{4}{3}\left[\varepsilon - (q^2 - q_0^2)^2\right],\tag{35}$$

where $\varepsilon - (q^2 - q_0^2)^2 > 0$ is the condition for instability of the uniform state $\psi = 0$. Second, there are two coupled amplitude equations corresponding to the modes $\mathbf{q}+\mathbf{Q}$ and $-\mathbf{q}+\mathbf{Q}$ for ψ_2 and ψ_3^*

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix}\begin{pmatrix} \psi_2(\omega) \\ \psi_3^*(\omega) \end{pmatrix} = 0,\tag{36}$$

where

$$a = -i\omega + (H+\Lambda_+)l_+ + \frac{3\psi_1^2}{4}\Lambda_+,\tag{37}$$

$$b = -Hl_- + \frac{3\psi_1^2}{4}\Lambda_+,\tag{38}$$

$$c = -Hl_+ + \frac{3\psi_1^2}{4}\Lambda_-,\tag{39}$$

$$d = -i\omega + (H+\Lambda_-)l_- + \frac{3\psi_1^2}{4}\Lambda_-.\tag{40}$$

where H vanishes if $\mathbf{Q} \parallel \mathbf{q}$ or is given by Eq. (34) if $\mathbf{Q} \perp \mathbf{q}$, and we have defined

$$\Lambda_\pm = \Lambda_{ij}(q_i \pm Q_i)(q_j \pm Q_j),\tag{41}$$

$$l_{\pm} = (|\mathbf{q} \pm \mathbf{Q}|^2 - q_0^2)^2 - (q^2 - q_0^2)^2. \tag{42}$$

Additionally, there are two more amplitude equations for modes $-\mathbf{q} - \mathbf{Q}$ and $\mathbf{q} - \mathbf{Q}$ leading to equations for ψ_2^* and ψ_3 that are just the complex conjugates of Eq. (36). The perturbation considered is linearly stable if the frequency ω is negative and pure imaginary. The imaginary frequencies are the decay rates, and they are obtained by solving the characteristic equation of the 2×2 matrix in Eq. (36).

When $\mathbf{Q} \parallel \mathbf{q}$ (permeation mode) there is no hydrodynamic coupling effect ($H = 0$), and $\Lambda_{\pm} = \bar{\Lambda}_L(q^2 + Q^2)$. From Eq. (36) we find two relaxation rates

$$\tau_{\parallel,1}^{-1} = \frac{3}{2}\bar{\Lambda}_L \psi_1^2 q^2 + \bar{\Lambda}_L \left[\frac{3}{2}\psi_1^2 + 2(11q^2 - 9q_0^2)q^2 + \frac{32}{3}(q^2 - q_0^2)^2 q^4 \psi_1^{-2} \right] Q^2 + \mathcal{O}(Q^4), \tag{43}$$

$$\tau_{\parallel,2}^{-1} = \bar{\Lambda}_L \left[2(3q^2 - q_0^2)q^2 - \frac{32}{3}(q^2 - q_0^2)^2 q^4 \psi_1^{-2} \right] Q^2 + \mathcal{O}(Q^4), \tag{44}$$

The relaxation rate $\tau_{\parallel,1}^{-1}$ describes the decay of the perturbation amplitude, whereas $\tau_{\parallel,2}^{-1}$ describes the decay of its phase. Due to the order one term in $\tau_{\parallel,1}^{-1}$ the amplitude decays much faster than the phase, and follows adiabatically any change in the phase. The longitudinal phase relaxation is diffusive ($\sim Q^2$), and depends only on $\bar{\Lambda}_L$. Since $\Lambda_L = \Lambda_I + 2\Lambda_A/3$ in dimensional units, the effect of anisotropic mobility is to enhance (reduce) diffusion if $0 < \Lambda_A < 3$ ($-3/2 < \Lambda_A < 0$).

When $\mathbf{Q} \perp \mathbf{q}$, we have $l_{\pm} = 2(q^2 - q_0^2)Q^2 + Q^4$, and $\Lambda_{\pm} = \bar{\Lambda}_L q^2 + \bar{\Lambda}_T Q^2$. Then it is straightforward to obtain two relaxation rates

$$\tau_{\perp,1}^{-1} = \frac{3}{2}\bar{\Lambda}_L \psi_1^2 q^2 + \left[2\bar{\Lambda}_L(q^2 - q_0^2)q^2 + \frac{3}{2}\psi_1^2 \bar{\Lambda}_T \right] Q^2 + \mathcal{O}(Q^4), \tag{45}$$

$$\tau_{\perp,2}^{-1} = 4h_{\perp}(q^2 - q_0^2) + 2\left[h_{\perp} + \bar{\Lambda}_L(q^2 - q_0^2)q^2 \right] Q^2 + \left[\bar{\Lambda}_L q^2 + 2\bar{\Lambda}_T(q^2 - q_0^2) \right] Q^4 + \mathcal{O}(Q^6), \tag{46}$$

where

$$h_{\perp} = H_{\perp}Q^2 = \frac{2}{3}\frac{\zeta}{1 + \alpha_{56}}q^2 \left[\varepsilon - (q^2 - q_0^2)^2 \right]. \tag{47}$$

As in the permeation mode, $\tau_{\perp,1}^{-1}$ and $\tau_{\perp,2}^{-1}$ govern the relaxation of the amplitude and phase

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respectively. Transverse mobility (terms in $\bar{\Lambda}_T$) contributes at order Q^2 to $\tau_{\perp,1}^{-1}$, and at order Q^4 to $\tau_{\perp,2}^{-1}$. These terms are negligible in the limit of small Q. On the other hand, as was the case for longitudinal distortions, there is a modification of the decay rates as they explicitly depend on the longitudinal mobility $\bar{\Lambda}_L$ rather than on the isotropic mobility Λ_I. Second, hydrodynamic flow couples to the phase of the perturbation and modifies its rate of decay as compared to the purely diffusive case. Interestingly, hydrodynamic decay dominates diffusive decay in the limit of small Q. It is only for larger values of Q that the conventional diffusive relaxation rate is recovered ($\sim Q^4$ for a transverse perturbation).

It is therefore of interest to examine the magnitude of the crossover length scale separating hydrodynamic and diffusive dominated relaxation. This scale may be relevant in the study of the relaxation of multi domain samples[34] as the present analysis suggests that hydrodynamic effects could be dominant as the linear scale of the microstructure grows. From Eq. (46), and assuming that the local wavenumber q relaxes to q_0 on a faster scale, we define a cross over length λ_c as

$$\lambda_c^2 = \frac{\bar{\Lambda}_L q^2}{2h_\perp}. \tag{48}$$

Hydrodynamic relaxation dominates at long wavelengths $\lambda_c Q \ll 1$, whereas hydrodynamic flow becomes negligible compared to order parameter diffusion otherwise. Furthermore, if $\mathbf{q} = \mathbf{q}_0$, the diffusion mode becomes identical to the undulation mode of a Smectic A liquid crystal (with a decay rate $\propto Q^4$).[33] In the hydrodynamically dominated regime $\lambda_c Q \ll 1$, the decay rate is proportional to Q^2 instead.

In order to estimate the crossover length λ_c, we first rewrite it in dimensional units

$$(\lambda_c^*)^2 = \frac{\Lambda_L(\alpha_4 + \alpha_{56})}{\psi_1^2}. \tag{49}$$

Since we do not have direct information about Λ_L, for the purpose of the estimate we just assume that it is of the same order as Λ_I as given by the non local Onsager coefficient for a binary

homopolymer mixture derived in[35–37]

$$\lambda(k) = \frac{6f(1-f)R_g^2}{\tau_0 N} g(1, k^2 R_g^2), \tag{50}$$

where f is the overall equilibrium composition, R_g the radius of gyration of the copolymer, and τ_0 a microscopic relaxation time for a single segment. N the degree of polymerization, and $g(x)$ the Debye function. The microscopic relaxation time for a segment of statistical length b is $\tau_0 = 6\pi b^3 \eta / k_B T$, with η being an effective shear viscosity.[35] This assumes Stokesian dynamics for a spherical particle of radius b. By using the fact that the Debye function in $\lambda(k)$ decays exponentially with a length scale R_g, we find

$$\Lambda_I \simeq R_g^3 \frac{\lambda(k)}{k_B T} \sim \frac{R_g^2 N^{1/2}}{\eta}. \tag{51}$$

If we further assume that $\eta = \alpha_4 + \alpha_{56}$, then $\Lambda_L(\alpha_4 + \alpha_{56}) \sim R_g^2 N^{1/2}$. Finally, the cross over length becomes

$$(\lambda_c^*)^2 \sim \frac{R_g^2 N^{1/2}}{\psi_1^2}, \tag{52}$$

For typical block copolymers the layer spacing q_0^{-1} is order of R_g,[12] and $(\lambda_c^*)^2 \sim N^{1/2}/q_0^2 \psi_1^2$. In the weak segregation limit of interest here, $\psi_1^2 \sim \varepsilon$, the reduced distance to the mean field order disorder transition so that $\lambda_c^* \sim R_g N^{1/4}/\sqrt{\varepsilon}$, and thus significantly larger than the lamellar spacing. In summary, flows at the scale of the lamellar spacing ($\sim R_g$) are strongly damped (as argued in Ref. 8), but dominate diffusive relaxation when $Q^{-1} > \lambda_c^* \sim R_g/\sqrt{\varepsilon}$ in the weak segregation regime.

We close this section by discussing the consequences of our analysis on scattering experiments. As already studied in Refs. 24–28, hydrodynamic effects on order parameter fluctuations manifest themselves in the structure factor which can be measured in a scattering experiment. In order to calculate the structure factor (and assuming that transverse diffusivity is negligible as shown

above), we add a thermal noise source to Eq. (23), which reduces to, in Fourier space,

$$\partial_t \psi + \left[v_i \partial_i \psi\right](\mathbf{k},t) + \Lambda_L (n_i k_i)^2 \left(\frac{\delta F}{\delta \psi}\right)(\mathbf{k},t) = \theta(\mathbf{k},t). \tag{53}$$

In this calculation we work in dimensional units. The noise term in Eq. (53) obeys

$$\left\langle \theta(\mathbf{k},t)\theta(\mathbf{k}',t')\right\rangle = 2(2\pi)^3 k_B T (n_i k_i)^2 \Lambda_L \delta(\mathbf{k}+\mathbf{k}')\delta(t-t'), \tag{54}$$

with k_B being Boltzmann's constant. We now consider an order parameter fluctuation as $\delta\psi = \psi - \psi_s$ where the reference state is given by Eq. (20) with $\mathbf{q} = \mathbf{q}_0$ and $\psi_1^2 = 4r/3\xi q_0^4$. Moreover, since hydrodynamic flow does not affect longitudinal (permeation) modes, we consider only transverse perturbations with wavevector $\mathbf{Q}$. As shown in the linear stability analysis, the mode $\mathbf{q}_0 + \mathbf{Q}$ couples with the mode $-\mathbf{q}_0 + \mathbf{Q}$. We then have two coupled equations for $\psi(\mathbf{k}_1 = \mathbf{q}_0 + \mathbf{Q},t)$ and $\psi(\mathbf{k}_2 = -\mathbf{q}_0 + \mathbf{Q},t)$:

$$\partial_t \delta\psi(\mathbf{k}_1,t) + \left[h_\perp Q^2 + \Lambda_L q_0^2(4r + \xi Q^4)\right]\delta\psi(\mathbf{k}_1,t) - \left[h_\perp Q^2 - 4r\Lambda_L q_0^2\right]\delta\psi(\mathbf{k}_2,t) = \theta(\mathbf{k}_1,t), \tag{55}$$

$$\partial_t \delta\psi(\mathbf{k}_2,t) + \left[h_\perp Q^2 + \Lambda_L q_0^2(4r + \xi Q^4)\right]\delta\psi(\mathbf{k}_2,t) - \left[h_\perp Q^2 - 4r\Lambda_L q_0^2\right]\delta\psi(\mathbf{k}_1,t) = \theta(\mathbf{k}_2,t), \tag{56}$$

where, in dimensional units,

$$h_\perp = \frac{2}{3}\frac{\xi}{u(\alpha_4 + \alpha_{56})}q_0^2 r. \tag{57}$$

We can decouple these equations by introducing $\phi_1(\mathbf{Q},t) = [\psi(\mathbf{k}_1,t) + \psi(\mathbf{k}_2,t)]/\sqrt{2}$ and $\phi_2(\mathbf{Q},t) = [\psi(\mathbf{k}_1,t) - \psi(\mathbf{k}_2,t)]/\sqrt{2}$ as

$$\partial_t \phi_1(\mathbf{Q},t) + 8r\Lambda_L q_0^2 \phi_1(\mathbf{Q},t) = \eta_1(\mathbf{Q},t), \tag{58}$$

$$\partial_t \phi_2(\mathbf{Q},t) + 2h_\perp Q^2 \phi_2(\mathbf{Q},t) + \xi\Lambda_L q_0^2 Q^4 \phi_2(\mathbf{Q},t) = \eta_2(\mathbf{Q},t), \tag{59}$$

where the noise terms $\eta_1(\mathbf{Q},t) = [\theta(\mathbf{k}_1,t) + \theta(\mathbf{k}_2,t)]/\sqrt{2}$ and $\eta_2(\mathbf{Q},t) = [\theta(\mathbf{k}_1,t) - \theta(\mathbf{k}_2,t)]/\sqrt{2}$

satisfy

$$\langle \eta_{1,2}(\mathbf{Q},t)\eta_{1,2}(-\mathbf{Q},t')\rangle = 2Vk_BTq_0^2\Lambda_L\delta(t-t'), \tag{60}$$

and where V is the volume of system. Again the other pair of coupled equations of the modes $-\mathbf{q}_0 - \mathbf{Q}$ and $\mathbf{q}_0 - \mathbf{Q}$ are just the complex conjugates of Eq. (58) and Eq. (59). While the first equation for ϕ_1 describes the amplitude relaxation in the absence of distortion of the lamellar structure, from the second equation we can obtain the structure factor due to phase fluctuations. The solution of Eq. (59) is given by

$$\phi(\mathbf{Q},t) = \int_{-\infty}^{t} dt' \, \eta_2(t') \exp\left[-(t-t')\left(\xi\Lambda_L q_0^2 Q^4 + 2h_\perp Q^2\right)\right] \tag{61}$$

from which we obtain the structure factor for transverse perturbations

$$\lim_{t\to\infty}\langle \psi(\mathbf{Q})\psi(-\mathbf{Q})\rangle_\perp = \frac{k_BT}{\xi Q^4[1+2Q^{-2}(\lambda_c^*)^{-2}]} \sim \begin{cases} Q^{-2} & \text{for } Q\lambda_c^* \ll 1 \\ \\ Q^{-4} & \text{for } Q\lambda_c^* \gg 1 \end{cases} \tag{62}$$

As expected from Eq. (46), we find two different regimes: A hydrodynamic dominated region (with scattering proportional to Q^{-2}) and a diffusion dominated region (with scattering proportional to Q^{-4}). Close to the order disorder transition where our model is valid, $(\lambda_c^*)^2 \sim \psi_1^{-2}$, and the hydrodynamic dominated region in the structure factor becomes narrow and perhaps difficult to detect. We mention that the equilibrium structure factor of block copolymers in the lamellar phase has been measured (see, e.g., Ref. 38). An oval shaped diffraction peak was observed close to the order-disorder transition which was interpreted to be a manifestation of rippling of layers based on a calculation of quasi-static properties of lamellar block copolymer near the order-disorder transition.[39] This conclusion agrees with our results. However, the detailed dependence of the scattering intensity along the transverse direction has not been, to our knowledge, analyzed. We also point out that the hydrodynamic mediated relaxation would become apparent in transient measurements of the non equilibrium structure factor during coarsening of a multi domain configuration.
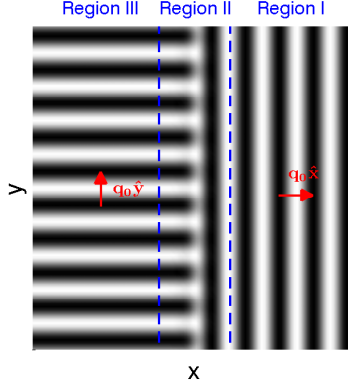
Figure 1: Sketch of a 90° tilt grain boundary separating two semi-infinite lamellae. In regions I and III the lamellae are nearly in their stationary state with wavevectors $q_0\hat{x}$ and $q_0\hat{y}$, respectively. The grain boundary region (II) is the region between the two blue dashed lines. In it, both envelopes A and B exhibit large variation.

Grain Boundary Motion

We have shown in the previous section that an anisotropic mobility tensor has only a small effect on the linear relaxation of a weakly perturbed lamellar phase. In general, however, when a block copolymer is brought below its microphase separation transition point, a large number of structural defects are quenched in a spatially extended system. These defects separate locally ordered domains of different orientations in an otherwise macroscopically disordered system. Within the defected region (the extent which is much larger that the lamellar wavelength in the weak segregation limit considered in this paper) undulation and permeation diffusive modes strongly couple. This coupling is expected to lead to a more significant contribution from anisotropic mobility to defect dynamics, the subject matter of this section.

We consider here a 90° tilt grain boundary that separates two semi-infinite domains of block copolymer lamellae with wavevector $q_0\hat{\mathbf{x}}$ in region I, and $q_0\hat{\mathbf{y}}$ in region III as shown in Figure 1. For simplicity, we focus on an effective two-dimensional system by taking advantage of translational symmetry along the $\hat{\mathbf{z}}$ direction, the direction perpendicular to the wavevectors of the two semi-infinite lamellae. We follow earlier work on grain boundary motion in layered systems as studied in other contexts such as Rayleigh-Bénard convection.[40–42]

In order to take into account the inhomogeneous nature of the kinetic mobility tensor Λ_{ij} within

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the interfacial region (region II in Figure 1) we introduce an auxiliary function $\Theta(x)$ that smoothly interpolates within the width of the grain boundary, from unity in the region where one semi-infinite lamella is present to zero in the other region,

$$
\begin{aligned}
\Lambda_{ij} &= \Theta(x)\Lambda_{ij}^{\mathrm{I}} + \Theta(-x)\Lambda_{ij}^{\mathrm{III}} \\
&= \Theta(x)\left[\delta_{ij} + \Lambda\left(\delta_{ix}\delta_{jx} - \frac{1}{3}\delta_{ij}\right)\right] + \Theta(-x)\left[\delta_{ij} + \Lambda\left(\delta_{iy}\delta_{jy} - \frac{1}{3}\delta_{ij}\right)\right],
\end{aligned}
\tag{63}
$$

where we have used Eq. (17). The constants $\Lambda_{ij}^{\mathrm{I}}$ and $\Lambda_{ij}^{\mathrm{III}}$ are the kinetic tensors defined in regions I and III with $q_0\hat{x}$ and $q_0\hat{y}$, respectively, and $\Theta(-x) = 1 - \Theta(x)$. This assumes that the microscopic mobility smoothly interpolates across a length scale proportional to the size of grain boundary. Since the width of the grain boundary diverges as $\varepsilon^{-1/2}$ in the weak segregation limit,[40,41] we infer that Λ_{ij} changes very slowly within the interfacial region. Due to the inhomogeneity of Λ_{ij} its gradient does not vanish, but $\partial_j\Lambda_{ij} = \Lambda\delta_{xj}\partial_x\Theta(x)$. Then, the order parameter equation becomes

$$
\partial_t\psi = \left\{\Lambda[\partial_x\Theta(x)]\partial_x + \Lambda_{ij}\partial_i\partial_j\right\}\left\{-\varepsilon\psi + \psi^3 + (\nabla^2 + q_0^2)^2\psi\right\}.
\tag{64}
$$

Advection is neglected in the analysis of this section. We now use a multiple scale analysis to derive amplitude equations close to the linear instability threshold ($\varepsilon \ll 1$). Following Tesauro and Cross,[41] we introduce slow variables $\bar{X} = \varepsilon^{1/4}x$, $X = \varepsilon^{1/2}x$, $Y = \varepsilon^{1/4}y$, $\bar{Y} = \varepsilon^{1/2}y$, $T = \varepsilon t$, and expand the derivatives $\partial_x \to \partial_x + \varepsilon^{1/4}\partial_{\bar{X}} + \varepsilon^{1/2}\partial_X$, $\partial_y \to \partial_y + \varepsilon^{1/4}\partial_Y + \varepsilon^{1/2}\partial_{\bar{Y}}$, and $\partial_t \to \varepsilon\partial_T$. Next, by noting that the order parameter scales as $\varepsilon^{1/2}$ we assume

$$
\psi = \frac{\varepsilon^{1/2}}{\sqrt{3}}\left[A\exp(iq_0x) + B\exp(iq_0y)\right] + \text{c.c.},
\tag{65}
$$

where A and B are functions of the slow variables only. Then the amplitude equations at $\mathscr{O}(\varepsilon^{3/2})$ are,

$$
\partial_T A = -q_0^2\left(1 + \frac{2}{3}\Lambda\right)\frac{\delta F'}{\delta A^*} + \Lambda\left[iq_0\partial_x\Theta(x) + q_0^2\Theta(-x)\right]\frac{\delta F'}{\delta A^*},
\tag{66}
$$

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$$\partial_T B = -q_0^2 \left(1 + \frac{2}{3}\Lambda \right) \frac{\delta F'}{\delta B^*} + \Lambda q_0^2 \Theta(x) \frac{\delta F'}{\delta B^*}, \tag{67}$$

where the free energy functional is given by

$$F'[A, A^*, B, B^*] = \int d^2 r \mathscr{F}'[A, A^*, B, B^*], \tag{68}$$

with the free energy density being

$$\mathscr{F}'[A, A^*, B, B^*] = -|A|^2 - |B|^2 + \frac{1}{2}\left(|A|^4 + |B|^4 \right) + 2|A|^2|B|^2$$
$$+ \left| (2iq_0\partial_x + \partial_y^2)A \right|^2 + \left| (2iq_0\partial_y + \partial_x^2)B \right|^2. \tag{69}$$

The stationary solutions A^s and B^s of a planar $90°$ grain boundary without anisotropy have been given in Refs. 40 and 41. Both A^s and B^s saturate to $\varepsilon^{1/2}$ as x tends to $+\infty$ or $-\infty$ respectively, but have different decaying behaviors within the grain boundary. The amplitude A^s has a longer decaying length scale $\sim \varepsilon^{-1/2}$ than B^s. Since the width of the grain boundary scales as $\varepsilon^{-1/2}$, it is reasonable to assume that this is the same scale of variation of the function $\Theta(x)$. This leads to $\partial_i \Lambda_{ij} \sim \varepsilon^{1/2}$, and its contribution to the amplitude equations appears at higher order in ε. The remaining relevant term is $\Lambda_{ij}\partial_i\partial_j(\delta F/\delta\psi)$, and Eq. (66) and Eq. (67) reduce to

$$\partial_T A = -q_0^2 \left\{ 1 + \frac{1}{3}\Lambda \left[2 + 3\Theta(-x) \right] \right\} \frac{\delta F'}{\delta A^*}, \tag{70}$$

$$\partial_T B = -q_0^2 \left\{ 1 + \frac{1}{3}\Lambda \left[2 + 3\Theta(x) \right] \right\} \frac{\delta F'}{\delta B^*}. \tag{71}$$

Hence the stationary solution of the amplitude equations remain unchanged by the anisotropy to lowest order in ε. Note that since $-3/2 < \Lambda < 3$, the coefficients of both $\delta F'/\delta A^*$ and $\delta F'/\delta B^*$ are positive.

We now use the energy method[40,43] to calculate the grain boundary velocity. The time deriva-

tive of F' is given by

$$\frac{dF'}{dt} = -\frac{2}{q_0^2}\int d^2r\frac{3}{3+\Lambda[2+3\Theta(-x)]}|\partial_t A|^2 - \frac{2}{q_0^2}\int d^2r\frac{3}{3+\Lambda[2+3\Theta(x)]}|\partial_t B|^2. \quad (72)$$

Note that any anisotropy effect is on the right hand side only. Assuming that the grain boundary moves with a constant velocity v_{GB}, we take $A^s(x - v_{\mathrm{GB}}t)$ and $B^s(x - v_{\mathrm{GB}}t)$ so that they are stationary in the moving frame. Then the time derivative can be replaced ∂_t with $-v_{GB}\partial_x$, and we find for the grain boundary velocity

$$v_{\mathrm{GB}} = M\int dy\left[\mathscr{F}'(x = \infty, y) - \mathscr{F}'(x = -\infty, y)\right], \quad (73)$$

and the effective mobility of the boundary is given by

$$\frac{1}{M} = \frac{2}{q_0^2}\int d^2r\frac{3}{3+\Lambda[2+3\Theta(-x)]}|\partial_x A^s|^2 + \frac{2}{q_0^2}\int d^2r\frac{3}{3+\Lambda[2+3\Theta(x)]}|\partial_x B^s|^2. \quad (74)$$

Since Λ is an order one quantity, the contribution to the boundary velocity due to anisotropic diffusion is large. The envelope A relaxes in region I (of dominant orientation $q_0\hat{x}$) differently than in region III (of dominant orientation $q_0\hat{y}$). In region I, diffusion is along the lamellar normal, whereas this component of the order parameter evolves through transverse diffusion in region III. Exactly the same is true of component B. As a consequence, the boundary velocity depends on a weighted average of the two independent mobility coefficients, with the weight function being the gradient of the order parameter envelopes, as given in Eq. (74). Of course, a similar qualitative behavior can be expected in the vicinity of other structural defects. When $\Lambda = 0$, the isotropic result of Refs. 40,42 is recovered.

We note that there is no grain boundary motion for unperturbed lamellae when $\mathscr{F}'(x = \infty) = \mathscr{F}'(x = -\infty) \sim \varepsilon$. In practice, an imbalance of the free energies caused by external sources is necessary to drive grain boundary motion so as to reduce excess free energy. We find that anisotropy enhances (reduces) v_{GB} when $0 < \Lambda_A < 3$ $(-3/2 < \Lambda_A < 0)$.

In conclusion, we have investigated diffusive and hydrodynamic driven relaxation of lamellar phases in block copolymers while allowing for uniaxial symmetry of the constitutive laws between forces and fluxes. We have shown that coupling to hydrodynamic flows leads to a relaxation rate proportional to Q^2, where Q is the wavenumber of the characteristic perturbation. This relaxation rate is faster than that arising from copolymer diffusion which is known to scale as Q^4 instead. The uniaxial symmetry of the lamellar phase requires an anisotropic mobility in the order parameter equation, and an anisotropic stress tensor in the momentum conservation equation. The effect of transverse mobility in general is negligible compared to either hydrodynamic flows or longitudinal order parameter diffusion for weakly perturbed lamellae. Hydrodynamic transport dominates diffusive relaxation when the wavevector of the perturbation is smaller than $\lambda_c^{-1} \sim \sqrt{\psi_1^2 / R_g^2 N^{1/2}}$. Finally, by studying the motion of a grain boundary we argue that defect velocities will be significantly affected by anisotropic diffusion.

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