EXTENDED CONSTITUTIVE LAWS FOR LAMELLAR PHASES

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ABSTRACT. Classically, stress and strain rate in linear viscoelastic materials are related by a constitutive relationship involving the viscoelastic modulus $G(t)$. This is an example within Linear Response Theory of relations between currents of conserved quantities and gradients of a complete set of their conjugate variables. The relations involve correlation functions of the currents in equilibrium. We explore the consequences of the latter relationship in the case of a mesoscale model of a block copolymer, and derive the resulting relationship between viscous friction and order parameter diffusion that would result in a lamellar phase. We also explicitly consider in our derivation the fact that the dissipative part of the stress tensor must be consistent with the uniaxial symmetry of the phase. We then obtain a relationship between the stress and order parameter autocorrelation functions that can be interpreted as an extended constitutive law, one that offers a route to determining them from microscopic experiment or numerical simulation.

1. INTRODUCTION

Modulated phases are equilibrium phases which in terms of symmetry are intermediate between disordered liquids and fully ordered crystalline solids. They are ubiquitous in soft-matter systems [1], and are currently being investigated for potential applications at the nanoscale, as well as for their role in biological materials. Their equilibrium state is characterized by a spatially periodic order parameter, with the modulation generally resulting from the competition between effective attractive interactions at short distances, and repulsive at long distances. The details of the competition determine both the symmetry of the phase and the characteristic length scale of its periodic structure. Dynamically, the response arising from the system's structural irreducible units introduces characteristic relaxation times that may span several disparate scales. Transport at any given scale is often viscoelastic as shorter scales do not completely decouple.

The main applications motivating our research concern the dynamical response of block copolymer phases to shears (rheology), and the nonequilibrium evolution of macroscopicallty disordered samples in the extended system limit. Applications of block copolymers in several areas of nanotechnology that leverage their self assembly has spurred a large body of experimental work [2]. Much of the equilibrium phenomenology is well understood theoretically and through simulation. The equilibrium free energy of the phases is determined through Self Consistent Field

Theory, a treatment that can include a fair amount of microscopic and architectural detail of the polymer chains [3, 4, 5]. In fact, block copolymer phases may well be a first example of a complex system in which a mesoscopic model allows a quantitative description of the equilibrium phase diagram. On the other hand, key aspects of their nonequilibrium behavior that are needed to optimize their processing, or to describe their rheology are not well understood.

A structured fluid in equilibrium possesses some degree of broken symmetry which is described by an appropriate mesoscopic order parameter set $\psi(\mathbf{x}, t)$. The equilibrium free energy F is then a functional of ψ and its gradients. Nonequilibrium evolution is often modeled as purely dissipative or relaxational, and assumed to be driven by free energy reduction,

$$\frac{\partial \psi}{\partial t} = -\Lambda \frac{\delta F}{\delta \psi}, \qquad F = \int d\mathbf{x} f(\psi, \partial_i \psi), \tag{1}$$

where Λ is an Onsager kinetic coefficient of microscopic origin, constant in some cases, or $\Lambda = -M\nabla^2$ if the order parameter satisfies a conservation law, with M a constant mobility. A number of well established methods exist that allow a quantitative determination of F at or near equilibrium. In the case of block copolymers, we mention Self Consistent Field Theory [6, 7, 4], and extensions of classical density functional theory [8, 9]. A self consistent calculation of the generalized chemical potential $\mu = \delta F/\delta \psi$ is obtained by computing the partition function of a single polymer chain in a self-consistently calculated chemical potential field (in the commonly used mean field version of the theories).

Recent extensions of Eq. (1) explicitly introduce the two point direct correlation function of the order parameter [10, 11]

$$C_2(\mathbf{x} - \mathbf{x}') = -\frac{1}{k_B T} \left(\frac{\delta^2 F}{\delta \psi(\mathbf{x}) \delta \psi(\mathbf{x}')} \right)_{\psi_0}, \tag{2}$$

where the derivative is computed around a reference state ψ_0, usually the equilibrium state. Gradient models of F in Eq. (1) are recovered by expanding the correlation function in gradients

$$C_2(\mathbf{x} - \mathbf{x}') = -\frac{1}{k_B T} \left(\hat{C}_0 + \hat{C}_2 \nabla^2 + \hat{C}_4 \nabla^4 + \ldots \right) \delta(\mathbf{x} - \mathbf{x}') \tag{3}$$

The correlation function determines the linear part of Eq. (1), to which non linearities are added phenomenologically. Different choices are now possible depending on whether ψ is a broken symmetry variable ($\hat{C}_0 = 0$ according to Goldstone's Theorem), the equilibrium phase is uniform in equilibrium (the Ginzburg-Landau free energy), or is modulated (the Brazovskii free energy, for example,[12, 13])

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

where q_0 is the characteristic wavenumber of the modulation, and r, u, and ξ are coefficients that depend on the system in question. These extensions have allowed quantitative descriptions of non uniform systems at the mesoscale.

In a formal expansion in frequency ($\omega = 0$ corresponds to equilibrium), the lowest order transport model must correspond to reversible (non dissipative or quasi static) motion. Incorporation of fluid flow requires consideration of an energy density that depends on kinetic energy $\frac{1}{2}\rho v^2$. The momentum density $\mathbf{g} = \rho \mathbf{v}$ and
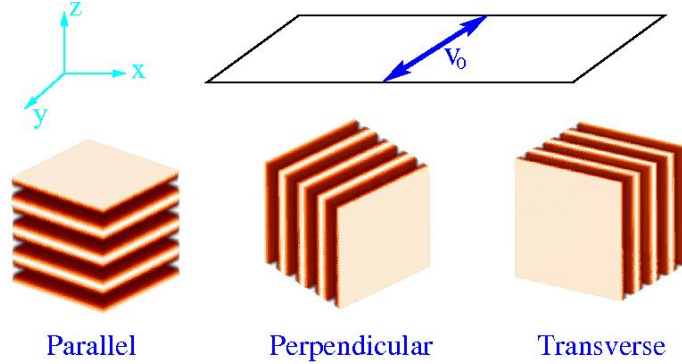
FIGURE 1. Schematic representation of the three possible lamellar orientations relative to a shear.

the velocity field $\mathbf{v}$ are then conjugate variables. Momentum density is a conserved variable, with stress its associated current, $\partial_t g_i + \partial_j \pi_{ij} = 0$. We will decompose the total stress as $\pi_{ij} = P\delta_{ij} - \sigma_{ij}^R - \sigma_{ij}^D$, explicitly separating the hydrostatic pressure P, and the reversible and dissipative contributions to π_{ij}. Advection of order parameter, $v_i \partial_i \psi$, can be added to Eq. (1) and carries with it the requirement to introduce a reversible stress in the momentum conservation equation through a Maxwell relation [14]

$$\frac{\partial \dot{\psi}}{\partial v_i} = \frac{\partial \dot{g}_i}{\partial(\partial_j \alpha_j)} \qquad \text{with} \quad \alpha_j = \frac{\partial f}{\partial(\partial_j \psi)}, \tag{5}$$

where the dot signifies time derivative. For example if, as is often the case, the energy density $f(\psi, \partial_i \psi)$ is quadratic in the order parameter gradient $f = \frac{K}{2}\|\nabla\psi\|^2 + g(\psi)$, a so called non standard reversible stress arises which is given by $\sigma_{ij}^R = K\partial_i \psi \, \partial_j \psi$. [15, 16]

Dissipative motion then appears formally at the next order in ω. In existing models of transport in modulated phases it arises from diffusive relaxation of $\psi(\mathbf{x}, t)$ in Eq. (1). In addition, viscous forces in the equation of conservation of momentum are introduced explicitly or implicitly through the dependence of the reversible body force $\partial_j \sigma_{ij}^R$ on ψ. Such a description is incomplete for partially fluid (modulated) phases. Consider, for example, the simplest modulated phase: a lamellar phase. Let $\hat{\mathbf{q}}$ be the normal to the lamellar planes, and assume that the system is subjected to a shear strain of amplitude γ. There are three possible orientations of the lamellar planes relative to the shear velocity $\mathbf{v}_0$ (Fig. 1): transverse ($\hat{\mathbf{q}} \parallel \mathbf{v}_0$), parallel ($\hat{\mathbf{q}} \parallel \nabla\mathbf{v}_0$), and perpendicular ($\hat{\mathbf{q}} \parallel \nabla \times \mathbf{v}_0$). As expected, shear along the transverse direction leads to an elastic stress linear in γ (solid-like response). Dissipation, however, can be shown to appear only nonlinearly (proportional to γ^3 for small γ). Furthermore, both parallel and perpendicular orientations are completely decoupled from the flow since $\hat{\mathbf{q}} \cdot \mathbf{v}_0 = 0$, and there is no effect from the shear. To remedy this lack of linear dissipation, a Newtonian constitutive law for a dissipative stress σ_{ij}^D is introduced [13, 17]. However, while linear in γ, this relation is not consistent with the symmetry of the phase, so that, for example, it does not distinguish, between locally parallel and perpendicular orientations.

We explore here a direct connection between order parameter relaxation and friction forces, and do so while allowing for a dissipative stress that is consistent with the uniaxial symmetry of the lamellar phase.

2. Theoretical Framework

2.1. **Linear Viscoelastic Modulus.** For an incompressible fluid of density ρ the equation of conservation of momentum reads

$$\rho \partial_t v_i + \partial_j \pi_{ij} = 0. \tag{6}$$

As indicated above, the reversible stress σ_{ij}^R is determined by the choice of gradient terms in the free energy, Eq. (5). However, one still needs to introduce a constitutive law for the dissipative stress σ_{ij}^D. In general, σ_{ij}^D is assumed to be linear in the small strain rate $v_{ij} = (\partial_i v_j + \partial_j v_i)/2$,

$$\sigma_{ij}^D = \eta_{ijkl}\, v_{kl}, \tag{7}$$

where η_{ijkl} is the viscosity tensor. The symmetry of the viscosity tensor needs to be compatible with the broken symmetry of the modulated phase. In the simple case of an isotropic incompressible Newtonian fluid, the coefficient of proportionality is constant, so that $\partial_j \sigma_{ij}^{\mathrm{D}} = \eta \partial^2 v_i$ where η is the shear viscosity.

More generally, a constitutive relation for viscoelastic fluids can be written as a generalization of Eq. (7) including non locality in both space and time [18]

$$\sigma_{ij}(\mathbf{x}, t) = \int_{-\infty}^{t} dt' \int d^3 x'\, G_{ijkl}(\mathbf{x} - \mathbf{x}', t - t') \Big[\partial_k' v_l(\mathbf{x}', t') + \partial_l' v_k(\mathbf{x}', t') \Big], \tag{8}$$

where $\partial_i' = \partial/\partial x_i'$, $\sigma_{ij} = \sigma_{ij}^{\mathrm{R}} + \sigma_{ij}^{\mathrm{D}}$ and $G_{ijkl}(\mathbf{x}, t)$ is the viscoelastic modulus. Because of causality the viscoelastic modulus is nonzero only for $t' < t$. The so called complex modulus is then defined as [18]

$$G_{ijkl}^*(\omega) = -i\omega \int_0^\infty dt\, e^{i\omega t} G_{ijkl}(t) = G_{ijkl}'(\omega) + i G_{ijkl}''(\omega), \tag{9}$$

where $G_{ijkl}'(\omega)$ is the storage modulus and $G_{ijkl}''(\omega)$ is the loss modulus. The number of independent elements of $G_{ijkl}(t)$ (or $G_{ijkl}^*(\omega)$) depends on the underlying broken symmetry of the modulated phase.

2.2. **Response Functions.** In Linear Response Theory, changes in a field in response to its conjugated external field are described through a response function. Strictly speaking, the relaxation modulus in Eq. (8) is not a response function because the strain rate is not the conjugate field to the shear stress, rather the strain tensor $u_{ij} = (\partial_i u_j + \partial_j u_i)/2$ is the appropriate variable. The response function relating stress to strain $\chi_{\sigma_{ij}\sigma_{kl}}(\mathbf{x}, t)$ is [19]

$$\sigma_{ij}(\mathbf{x}, t) = \int_{-\infty}^{t} dt' \int d^3 x'\, \chi_{\sigma_{ij}\sigma_{kl}}(\mathbf{x} - \mathbf{x}', t - t')\, [\partial_k' u_l(\mathbf{x}', t') + \partial_l' u_k(\mathbf{x}', t')], \tag{10}$$

where both temporal and spatial translation invariances are assumed. The response function $\chi_{\sigma_{ij}\sigma_{kl}}(\mathbf{x} - \mathbf{x}', t - t')$ is nonzero only for $t > t'$ because of causality. The Laplace transform is then

$$\chi_{\sigma_{ij}\sigma_{kl}}(\mathbf{x} - \mathbf{x}', z) = \int_0^\infty dt\, e^{izt} \chi_{\sigma_{ij}\sigma_{kl}}(\mathbf{x} - \mathbf{x}', t), \tag{11}$$

which is analytic in the upper half z-plane. Also, its half time Fourier transform is

$$\chi_{\sigma_{ij}\sigma_{kl}}(\mathbf{x} - \mathbf{x}', \omega) = \lim_{\epsilon \to 0} \chi_{\sigma_{ij}\sigma_{kl}}(\mathbf{x} - \mathbf{x}', z = \omega + i\epsilon), \tag{12}$$

which can be decomposed into real and imaginary parts

$$\chi_{\sigma_{ij}\sigma_{kl}}(\mathbf{x} - \mathbf{x}', \omega) = \chi'_{\sigma_{ij}\sigma_{kl}}(\mathbf{x} - \mathbf{x}', \omega) + i\chi''_{\sigma_{ij}\sigma_{kl}}(\mathbf{x} - \mathbf{x}', \omega). \tag{13}$$

Then, the fluctuation-dissipation theorem states that the imaginary part of the response function is related to the auto correlation function of the stress

$$\chi''_{\sigma_{ij}\sigma_{kl}}(\mathbf{k}, \omega) = \frac{\beta\omega}{2V} \langle \sigma_{ij}(\mathbf{k}, \omega)\sigma_{kl}(-\mathbf{k}, t = 0) \rangle, \tag{14}$$

where V is the volume of the system.

Of course, the viscoelastic relaxation modulus $G_{ijkl}(t)$ is related to the correlation function as well. First, noting that $v_i = \partial_t u_i$, we integrate Eq. (8) by parts to obtain

$$\begin{aligned}
\sigma_{ij}(\mathbf{x}, t) &= -\int_{-\infty}^{t} dt' \int d^3x' \, \partial_{t'} G_{ijkl}(\mathbf{x} - \mathbf{x}', t - t') \Big[\partial_k' u_l(\mathbf{x}', t') + \partial_l' u_k(\mathbf{x}', t') \Big] \\
&\quad + \int d^3x' \, G_{ijkl}(\mathbf{x} - \mathbf{x}', t = t') \Big[\partial_k' u_l(\mathbf{x}', t) + \partial_l' u_k(\mathbf{x}', t) \Big].
\end{aligned} \tag{15}$$

By comparing this equation with Eq. (10) we find

$$\chi_{\sigma_{ij}\sigma_{kl}}(\mathbf{x} - \mathbf{x}', t - t') = -\partial_{t'} G_{ijkl}(\mathbf{x} - \mathbf{x}', t - t') + G_{ijkl}(\mathbf{x} - \mathbf{x}', t - t')\delta(t' - t). \tag{16}$$

Since both $\chi_{\sigma_{ij}\sigma_{kl}}$ and G_{ijkl} are nonzero for $t > t'$ we take the Laplace transform of the above equation. Since boundary terms at $t = t'$ cancel out, and by using the fact that $\chi_{\sigma_{ij}\sigma_{kl}}(\mathbf{k}, \omega) = \lim_{\epsilon \to 0} \chi_{\sigma_{ij}\sigma_{kl}}(\mathbf{k}, z = \omega + i\epsilon)$ and the definition of the complex modulus Eq. (9) we find

$$\chi_{\sigma_{ij}\sigma_{kl}}(\mathbf{k}, \omega) = G^*_{ijkl}(\mathbf{k}, \omega). \tag{17}$$

In other words, the complex modulus is the momentum current autocorrelation function. In terms of this function, the storage and loss moduli are given by

$$G''_{ijkl}(\mathbf{k}, \omega) = \frac{\beta\omega}{2V} \langle \sigma_{ij}(\mathbf{k}, \omega)\sigma_{kl}(-\mathbf{k}, t = 0) \rangle, \tag{18}$$

$$G'_{ijkl}(\mathbf{k}, \omega) = \frac{\beta}{2V} \mathcal{P} \int_{-\infty}^{\infty} \frac{d\omega_1}{\pi} \frac{\omega_1 \langle \sigma_{ij}(\mathbf{k}, \omega_1)\sigma_{kl}(-\mathbf{k}, t = 0) \rangle}{\omega_1 - \omega}. \tag{19}$$

where we have used the fluctuation-dissipation theorem Eq. (14), and the Kramers-Kronig relation between χ' and χ''. In Eq. (19) $\mathcal{P}$ stands for the principal value of the integral. In short, Eqs. (18) and (19) show that a general, but linear, viscoelastic constitutive relation follows from the stress autocorrelation function. We also mention that the momentum conservation equation allows one to express the stress autocorrelation function in terms of the velocity autocorrelation function. In general, if the fluid is incompressible, one can use the longitudinal part (parallel to the velocity gradient) of the momentum conservation equation to eliminate the pressure, and from the resulting transverse part of the momentum conservation equation one finds

$$\langle v_i(\mathbf{k}, \omega)v_k(-\mathbf{k}, t = 0) \rangle = \frac{k_j k_l}{\rho^2 \omega^2} \langle \sigma_{ij}(\mathbf{k}, \omega)\sigma_{kl}(-\mathbf{k}, t = 0) \rangle. \tag{20}$$

By inserting Eq. (20) into Eq. (17), it is possible to relate the complex modulus to the velocity autocorrelation function.

The Green-Kubo relation follows immediately from Eq. (18). In the limit of small frequency and wavenumber, one has

$$\eta_{ijkl} = \lim_{\omega \to 0} \lim_{k \to 0} \frac{G''_{ijkl}(\mathbf{k}, \omega)}{\omega}, \tag{21}$$

which is the viscosity tensor defined in Eq. (7).

2.3. **Extended Constitutive Relations.** In the spirit of Eqs. (2) and (3), one can ask whether it is possible to use microscopic information contained in the stress autocorrelation function (for example, from experiments or molecular level simulation) to formulate extended constitutive equations for the stresses that will appear as nonlocal contributions in the momentum conservation equation. This is analogous to nonlocal contributions from the pair correlation function C_2 in the equation governing the evolution of the order parameter. Such a representation could be particularly useful in modulated phases in which structural correlations affect molecular friction.

If there exists a hydrodynamic variable associated with a broken symmetry, flow advects the new variable, and the reversible momentum current σ_{ij}^{R} contains an additional contribution associated with the restoring force to an equilibrium ordered state when the system is driven out of equilibrium, as shown in Eq. (5) [14]. Assume now that Eq. (8) remains valid. In general, the equation of conservation of momentum can be formally linearized as

$$\rho \partial_t v_i - \partial_j \sigma_{ij}^{\mathrm{D}} = -\partial_i P + \partial_j \sigma_{ij}^{\mathrm{R}}. \tag{22}$$

We rewrite this equation, in Fourier space,

$$\hat{\mathcal{L}}_{ij}(\mathbf{k}, \omega) v_j(\mathbf{k}, \omega) = \hat{\mathcal{F}}_i(\psi), \tag{23}$$

where the linear operator $\hat{\mathcal{L}}_{ij}(\mathbf{k}, \omega)$ is defined from the LHS of Eq. (22), and $\hat{\mathcal{F}}_i(\psi)$ follows from the dependence of the reversible shear stress on the additional order parameter fields. The velocity auto correlation function can be formally written as

$$\langle v_i(\mathbf{k}, \omega) v_k(-\mathbf{k}, t = 0) \rangle = \hat{\mathcal{L}}_{ij}^{-1}(\mathbf{k}, \omega) \hat{\mathcal{L}}_{kl}^{-1}(-\mathbf{k}, -\omega) \langle \hat{\mathcal{F}}_j(\psi)(\mathbf{k}, \omega) \hat{\mathcal{F}}_l(\psi)(-\mathbf{k}, t = 0) \rangle, \tag{24}$$

where $\hat{\mathcal{L}}^{-1}(\mathbf{k}, \omega)$ is the inverse of $\hat{\mathcal{L}}(\mathbf{k}, \omega)$ such as $\hat{\mathcal{L}}_{ij}^{-1}(\mathbf{k}, \omega) \hat{\mathcal{L}}_{jk}(\mathbf{k}, \omega) = \delta_{ij}$. Note now that, in the linear regime, the RHS of Eq. (24) is proportional to the autocorrelation function of the order parameter. Equation (24) is interesting as it shows the formal relationship between correlations of the viscous degrees of freedom (and hence momentum response), and the structural order parameters that characterize the mesophase. As such, it can be thought of as a generalized constitutive equation. We next illustrate the relationship in the specific case of a block copolymer in the lamellar phase.

3. Viscoelastic Response of a Lamellar Phase

Diblock copolymers are macromolecules comprising two chemically distinct and mutually incompatible segments (monomers) that are covalently bonded. Their equilibrium properties are dictated by N, the degree or polymerization (i.e., the length of the chain), f, the volume fraction of one of the monomers, and χ, the Flory-Huggins interaction parameter between the distinct segments [4]. The first two parameters can be controlled through processing, whereas the third is determined by the choice of monomers involved. Above an order-disorder transition

temperature T_{ODT}, the equilibrium phase is fluid like (disordered). Below T_{ODT}, equilibrium structures of a wide variety of symmetries have been predicted and experimentally observed. Around $f = 0.5$ (symmetric mixture), a so called lamellar phase is observed, in which nanometer sized layers of A and B rich regions alternate in space. Phases of complex symmetries, including bi-continuous structures, have been predicted and observed in higher order multiblocks [20, 21].

At frequencies low compared with the smallest inverse relaxation time of the polymer, chain conformation fluctuations can be adiabatically eliminated, and a mesoscopic theory can be developed. The evolution of a melt is described by an order parameter field $\psi(\mathbf{x}, t)$ which represents the local density difference of the constituent monomers. The coarse grained free energy functional F was first given by [12]. In the weak segregation limit near the order-disorder transition point, the simpler free energy in Eq. (4) has been introduced [13, 22].

The linearized momentum conservation equation describing the dynamics of block copolymer in lamellar phases is given by Eq. (22), with the reversible stress tensor given by

$$\partial_j \sigma_{ij}^{\mathrm{R}} = -\psi \partial_i \left(\frac{\delta F}{\delta \psi} \right). \tag{25}$$

We now introduce the following constitutive law for the dissipative stress tensor σ_{ij}^{D} that is compatible with the uniaxial symmetry of a lamellar phase. For perfectly ordered lamellae with $\hat{q}$ being the unit normal to the layers, we have[23]

$$\sigma_{ij}^{\mathrm{D}} = \alpha_1 \hat{q}_i \hat{q}_j \hat{q}_k \hat{q}_l v_{kl} + \alpha_4 v_{ij} + \alpha_{56} \hat{q}_k (\hat{q}_i v_{kj} + \hat{q}_j v_{ki}), \tag{26}$$

where α_1, α_4 and α_{56} are viscosity coefficients. Now we can use this momentum conservation equation to derive a relation in terms of the autocorrelation function of the order parameter.

As a reference state we consider one in which flow is absent, and planar lamellae with periodicity $\mathbf{q}$ are stationary. The function $\psi_0 = \psi_1 \cos(\mathbf{q} \cdot \mathbf{x}) + \ldots$ minimizes the free energy Eq. (4) to lowest order in $r/\xi q_0^4 \ll 1$ in the weak segregation regime close to T_{ODT}, with

$$\psi_1^2 = \frac{4}{3} \left[\frac{r}{u} - \frac{\xi}{u} (q^2 - q_0^2)^2 \right]. \tag{27}$$

Next, we consider disturbances from the reference state as $\delta\psi = \psi - \psi_0$ and v_i, and linearize Eq. (22), resulting in

$$\rho \partial_t v_i = \partial_j \delta\sigma_{ij}^{\mathrm{R}} + \partial_j \sigma_{ij}^{\mathrm{D}}, \tag{28}$$

where

$$\partial_j \delta\sigma_{ij}^{\mathrm{R}} = -\psi_0 \partial_i \left[\bar{\mu}(\mathbf{r}) \delta\psi \right]. \tag{29}$$

with $\bar{\mu}(\mathbf{r}) = -r + 3u\psi_0^2 + \xi(\nabla^2 + q_0^2)^2$. We can then identify the linear operator $\hat{\mathcal{L}}_{ij}$ from the terms proportional to the flow velocity in Eq. (28),

$$\hat{\mathcal{L}}_{ij}(\mathbf{k}, \omega) v_j(\mathbf{k}, \omega) = -i\omega\rho v_i(\mathbf{k}, \omega) - \partial_j \sigma_{ij}^{\mathrm{D}}(\mathbf{k}, \omega), \tag{30}$$

and

$$\hat{\mathcal{F}}_i(\psi) = \partial_j \delta\sigma_{ij}^{\mathrm{R}}. \tag{31}$$

The resulting relation is a function of the orientation of the lamellae relative to the local velocity gradient. To be specific, we consider two examples: Perpendicularly and transverse oriented lamellae (Fig. 1).

3.1. **Perpendicular Orientation.** In this case $\mathbf{v} = v\hat{x}$, $\mathbf{q} = q\hat{y}$, $\mathbf{k} = k\hat{z}$, and there is no reversible contribution to the stress tensor because $\partial_j \delta\sigma_{ij}^{\mathrm{R}} \propto k_i - q_i$ is perpendicular to v_i. Then Eq. (28) when linearized reduces to

$$\rho\partial_t v(\mathbf{k}, t) = -\frac{\alpha_4}{2} k^2 v(\mathbf{k}, t). \tag{32}$$

Now it is straight forward to calculate the velocity-velocity correlation function. First, we Laplace transform Eq. (32) to get

$$v(\mathbf{k}, z) = \frac{1}{-iz + \alpha_4 k^2/2\rho} v(\mathbf{k}, t = 0). \tag{33}$$

This equation and Eq. (3.14) of Ref. [19] imply that

$$\chi_{vv}(\mathbf{k}, z) = \frac{\alpha_4 k^2/2\rho}{-iz + \alpha_4 k^2/2\rho} \chi_{vv}(\mathbf{k}). \tag{34}$$

Since $\chi_{vv}(\mathbf{k}, \omega) = \lim_{\epsilon \to 0} \chi_{vv}(\mathbf{k}, z = \omega + i\epsilon) = \chi'_{vv}(\mathbf{k}, \omega) + i\chi''_{vv}(\mathbf{k}, \omega)$ and $\chi_{vv}(\mathbf{k}) = \rho^{-1}$ we find from Eqs. (18) and (19) that

$$G'_{xzxz}(\mathbf{k}, \omega) = \frac{\alpha_4}{2}\omega^2 \frac{\alpha_4 k^2/2\rho}{\omega^2 + (\alpha_4 k^2/2\rho)^2}, \tag{35}$$

and

$$G''_{xzxz}(\mathbf{k}, \omega) = \frac{\alpha_4}{2} \frac{\omega^3}{\omega^2 + (\alpha_4 k^2/2\rho)^2}. \tag{36}$$

The viscosity coefficient can be obtained by taking small k and ω limits

$$\eta_\perp = \lim_{\omega \to 0} \lim_{k \to 0} \frac{G''_{xzxz}(\mathbf{k}, \omega)}{\omega} = \frac{\alpha_4}{2}. \tag{37}$$

The lamellar phase in this orientation responds as a terminal fluid of shear viscosity α_4 (terminal behavior has at low frequencies $G''_{xzxz} \propto \omega$ and $G'_{xzxz} \propto \omega^2$). This is an obvious result and illustrates that there is no coupling between the order parameter and the fluid velocity within this description. The same is the case for the parallel orientation. Interestingly, however, the resulting viscosity in this case is $\alpha_4 + \alpha_{56}$. Even though the lamellar phase responds as a terminal fluid for both orientations, the resulting viscosity is nevertheless different.

3.2. **Transverse Orientation.** Consider now a transverse orientation in which $\mathbf{v} = v\hat{x}$, $\mathbf{q} = q\hat{x}$ and $\mathbf{k} = k\hat{z}$. In contrast to the perpendicular orientation, since $\mathbf{v} \parallel \mathbf{q}$, $\hat{F}_x(\psi) \propto q_x$ does not vanish, and there exists coupling between ψ and $\mathbf{v}$. Elastic and viscous response are coupled in this case. If we use the incompressibility condition ($\mathbf{v} \cdot \mathbf{k} = 0$), we find

$$\hat{\mathcal{L}}_{xx} = -i\omega\rho + \frac{\alpha_4 + \alpha_{56}}{2} k^2, \tag{38}$$

and

$$\hat{\mathcal{F}}_x(\psi) = iq\frac{\psi_1}{2}\xi\Big[k^4 + 2k^2(q^2 - q_0^2)\Big]\Big[\delta\psi(\mathbf{k} - \mathbf{q}, t) - \delta\psi(\mathbf{k} + \mathbf{q}, t)\Big]. \tag{39}$$

Defining the phase of the perturbation $\phi_2(\mathbf{k}, t) = [\delta\psi(\mathbf{k} + \mathbf{q}, t) - \delta\psi(\mathbf{k} - \mathbf{q}, t)]/\sqrt{2}$, we find from Eqs. (18), (20) and (24),

$$\begin{aligned} G'_{xzxz}(\mathbf{k}, \omega) = &-\frac{\beta}{V}\frac{\psi_1^2}{4}q^2\xi^2 k^2\Big[k^2 + (q^2 - q_0^2)\Big]^2 \\ &\times \mathcal{P}\int_{-\infty}^{\infty}\frac{d\omega_1}{\pi}\frac{\omega_1^3\langle\phi_2(\mathbf{k}, \omega_1)\phi_2(-\mathbf{k}, t = 0)\rangle}{(\omega_1 - \omega)[\omega_1^2 + (\alpha_4 + \alpha_{56})^2 k^4/4\rho^2]}, \end{aligned} \tag{40}$$

and

$$\frac{G''_{xzxz}(\mathbf{k},\omega)}{\omega} = -\frac{\beta}{V}\frac{\psi_1^2}{4}q^2\xi^2k^2\Big[k^2 + 2(q^2 - q_0^2)\Big]^2\frac{\omega^2\langle\phi_2(\mathbf{k},\omega)\phi_2(-\mathbf{k},t=0)\rangle}{\omega^2 + (\alpha_4 + \alpha_{56})^2k^4/4\rho^2}. \quad (41)$$

Equations (40) and (41) directly relate the viscoelastic modulus and the order parameter correlation function. Of course, their specific form here depend on the functional form of the reversible stress and of the dissipative stress tensor chosen (the prefactor and denominator in both equations respectively). The prefactor is related to the equilibrium inverse susceptibility of the order parameter (not any kinetics), and the denominator indicates viscous diffusion with viscosity $\alpha_4 + \alpha_6$. It is quite straightforward to conduct the calculation for other free energies or forms of the dissipative stress. Assuming, however, that both functions can be experimentally determined (e.g., micro rheology and X-Ray scattering) or by numerical simulation of a copolymer melt, including dynamical density functional theory, their relationship would give information about the microscopic mechanisms responsible for viscous friction. These mechanisms are, at present, unknown for block copolymers, fact that hinders a solid theoretical understanding of their nonequilibrium evolution, and, as indicated in the Introduction, underpins the need for a great deal of empiricism in their processing.

4. Acknowledgments

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