PHYSICAL REVIEW E VOLUME 48, NUMBER 5 NOVEMBER 1993

# Dynamical theory of concentration fluctuations in polymer solutions under shear

Scott T. Milner
*Exxon Research and Engineering, Annandale, New Jersey 08801*
(Received 3 December 1992)

Shear flow has been shown experimentally to lead to large concentration fluctuations in entangled polymer solutions near to their coexistence curves. I develop a dynamical theory of concentration fluctuations coupled to polymer elastic stress, in terms of a "two-fluid" model of polymer plus solvent. At first order in shear rate $\dot{\gamma}$, only one component of the stress is coupled to the concentration. The structure factor $S(q;\dot{\gamma})$ is given as a "history integral" over thermal-noise amplitudes at wave numbers convected onto $q$. The characteristic wave number $q^*$, at which concentration fluctuations relax in a stress-relaxation time, determines (1) the length scale for the mixing of modes as observed in the dynamic light scattering of quiescent solutions, and (2) the length scale of peaks observed in static light scattering under shear. Both features depend on treating stress dynamics beyond an adiabatic approximation. At $O(\dot{\gamma}^2)$, the spinodal is shifted to higher (lower) temperatures for fluctuations in the gradient (vorticity) direction.

PACS number(s): 61.25.Hq

Moderately concentrated polymer solutions under shear flow show a host of remarkable properties; their striking rheological behavior in a multitude of situations has been widely studied. In the great majority of these studies, the concentration of the polymer in the solution is or is assumed to be spatially uniform. In some regimes, however, particularly for entangled solutions not too far from their coexistence curves, shear flow couples strongly to concentration fluctuations.

This behavior has been explored experimentally by several groups, beginning with observations of increased turbidity of entangled polymer solutions in near-$\theta$ solvents when the solutions were forced through capillaries [1]. This effect was attributed by those who first observed it to a shift in the spinodal temperature induced by the Poiseuille flow.

More recently, several groups [2–7] have studied static and dynamic light scattering from similar solutions under well-characterized rheometric shear flows. Among the striking experimental results recently obtained [2], the solutions were seen to scatter light most strongly at a finite wave vector, corresponding to a characteristic size for concentration fluctuations of several thousand angstroms, at shear rates comparable to the stress-relaxation rate $\tau^{-1}$ of the solutions. Enhanced forward scattering—characteristic of an incipient phase separation—was observed only at higher shear rates, and even then the light scattering was strongest at a finite wave vector.

The relaxation of the light scattering to the quiescent behavior was also recently studied [3]. The time dependence of the relaxation of the structure factor from its steady-state value under shear to its quiescent equilibrium value was shown to be closely related to the striking behavior first observed in dynamic light scattering from quiescent solutions by Adam and Delsanti [8]. They saw two characteristic relaxation rates for concentration fluctuations of a given wave number, with a dispersion relation suggestive of two coupled modes. Their results were in accord with a simple theory of Brochard and de Gennes of an entangled polymer solution as a "transient gel," which behaves as a simple two-fluid mixture on time scales long compared to $\tau$, and as a solvated gel on shorter time scales [9]. Associated with this crossover in behavior with time scale is a "magic length" $l_m \sim (D\tau)^{1/2}$, above which concentration fluctuations decay by diffusion with diffusion coefficient $D$ as in a simple two-fluid mixture. Concentration fluctuations of size less than $l_m$ cause stresses in the entangled polymer network before they dissipate.

In this paper, I will describe a dynamical theory of coupled concentration and stress fluctuations in a polymer solution under shear flow, as a pair of coupled Langevin equations. In such a theory, thermal-noise sources constantly produce fluctuations, which are convected by the shear flow and decay in response to thermodynamic forces. The dynamical steady state of birth, convection, and death of fluctuations gives rise to the structure factor.

The model described in this paper has several important antecedents. In the absence of shear flow, the model is consistent with the Brochard–de Gennes description [9]; the coupling of stress and concentration of a transient gel is the means by which shear flow, which generates stress, can cause the growth of concentration fluctuations, as observed in the experiments.

For sufficiently slow processes, at wave numbers sufficiently small that the stress in the entangled network relaxes quickly to a value consistent with local equilibrium, the present model reduces essentially to that given by Helfand and Fredrickson (HF) [10]; similar approaches have also been taken by Doi [11], Onuki [12], and the present author [13]. In the HF model, the stress is coupled to the concentration, but the evolution of the stress is taken to be adiabatically determined, i.e., the stress is given by a constitutive relation.

This approximation fails at sufficiently large wave numbers and short time scales that the stress cannot follow the birth and death of concentration fluctuations; the crossover wave number is none other than $q^* \sim l_m^{-1}$, the inverse of the "magic length." The inhomogeneous stresses cannot faithfully follow the concentration fluctuations at shorter length scales, which lessens the efficiency of the HF mechanism for shear-enhanced concentration fluctuations. Thus the magic length also turns out to be the length scale of the peak observed in static light scattering by Wu, Pine, and Dixon [2].

This paper is organized in five sections, as follows. In Sec. I, I present general considerations leading to a pair of coupled Langevin equations describing concentration and strain fluctuations. The ingredients for this formulation are a two-fluid model of polymer plus solvent inspired by theories of flow in porous media [14] and the Brochard–de Gennes theory; Galilean invariance, which determines the form of the convective terms for the strain; the result from Doi-Edwards theory that stress relaxation in entangled systems is approximately single exponential even in the nonlinear regime [15]; and Onsager reciprocity [16].

In Sec. II, the results of the adiabatic approximation are reviewed; simple estimates are obtained of the sign and size of the effect of shear on concentration fluctuations. The structure factor, including effects of affine convection, is computed as a "history integral" over the lifetime of fluctuations. The HF mechanism for growth of fluctuations is described in real and reciprocal space, using the two-fluid model.

In Sec. III, the stress dynamics are retained, and arguments for the characteristic length scale of the observed peak in the structure factor are given. A simplified model at low shear rate involving a single component of the strain tensor is obtained. This model maps onto the Brochard–de Gennes theory; the resulting mixed hydrodynamic modes are displayed.

In Sec. IV, numerical results for the structure factor are obtained by computing a discretized history-integral expression for the matrix of correlation functions; the magnitude, width, and location of the scattering peak are displayed. The arguments of the previous section as to the effects of affine convection and stress dynamics are checked by artificially turning off the convection term and forcing the adiabatic approximation at all wave numbers. The transient response of the structure factor after cessation of shear is explored.

In Sec. V, limitations and possible extensions of the present theory are explored, including saturation effects (breakdown of small-fluctuation approximation), effect of higher shear rates (shear thinning), and effects of normal stresses on the location of the spinodal [11].

## I. MODEL FORMULATION

### A. Dynamical theory

To describe the effect of imposed shear flow on concentration and other fluctuations in a polymer solution, a dynamical theory is required. Shear flow is not analogous to a thermodynamic potential, such as an orienting potential acting on the bonds of the polymer. The static structure factor results from a dynamical steady state, in which random thermal forces create fluctuations, which are convected by the shear flow and decay by diffusion.

A description of a fluctuating system with imposed shear flow can be given in terms of coupled Langevin equations for the long-lived variables of interest. Generally, the long-lived variables included in such a theory are hydrodynamic or broken-symmetry degrees of freedom [16]. At long wavelengths, these variables relax at rates that vanish as some power of the wave number. The relaxation rates are slow either because some quantity must be transported a large distance (conservation law), or because a long-wavelength distortion of the variable costs very little free energy (broken symmetry).

This approach has been carried out for demixing simple fluids under shear [17]. In that problem, the important long-lived fluctuating quantities are the concentration difference from its average value and the variations in the velocity field itself about the imposed mean flow. The problem is appropriately simplified by assuming the fluids are incompressible, which eliminates the density and the longitudinal part of the velocity from the set of long-lived variables.

### B. Strain as a variable

Because only the relaxation rates of the few conserved or broken-symmetry variables vanish in the limit of long wavelengths, at low frequencies a separation of time scales exists between the relaxation rates of the few long-lived variables and all other variables [16]. Such theories of hydrodynamic fluctuations are valid for wave numbers and frequencies sufficiently small that all but the long-lived degrees of freedom have reached local equilibrium. For a solution with sufficiently long and entangled polymer chains, the time for elastic stress to relax may be extremely long. This means the hydrodynamic theory is only valid for frequencies less than the stress relaxation rate, i.e., for frequencies so low that the polymer solution is Newtonian.

To increase the range of frequencies in which the model is valid, some new dynamical variable corresponding to fluid stress or fluid strain must be added to the set of long-lived variables. This must be done even though the stress-relaxation time does not vanish in the limit of long wavelengths. In solids, the strain field is a broken-symmetry variable, since uniform translation leaves the free energy unchanged. In a liquid, translational symmetry is not broken, so that with sufficient time, stresses relax and strains are not defined. However, on time scales short compared to the stress-relaxation time, the strain in a fluid may be a more or less well-defined quantity. Physically, the strain in a fluid corresponds to the deformation, which, if it were made instantaneously, would relax the stress.

Because the stress in a polymer solution is not hydrodynamic, separation of time scales cannot be invoked to limit the number of variables in the theory, once stress is included. That is, there are other degrees of freedom, for instance, higher moments of the distribution of bond orientations, which relax on time scales comparable to the stress-relaxation time. These degrees of freedom are neglected in what follows for two reasons. First, as shown below, the equation of motion for polymer concentration fluctuations couples quite generally to the polymer elastic stress tensor. Second, reasonable equations of motion for the elastic stress tensor itself can be written without coupling to the neglected variables.

### C. Two-fluid model

Several approaches are available to derive the form of the coupled Langevin equations for polymer concentration, polymer strain, and velocity perturbations about the mean shear flow. One systematic approach, partially carried out [13] for the case of polymer chains described by the Rouse model [18] of microscopic dynamics, is based on projection operator techniques [19]. This method, though cumbersome, does formally produce Langevin equations of canonical form for a set of long-lived variables, from the microscopic Langevin equation describing a Rouse chain in a shear flow acted upon by thermal forces. I shall not pursue this approach here.

There are in addition two phenomenological approaches to writing the desired Langevin equations. The first is simply to write the most general allowed form based on symmetry arguments, Galilean invariance, Onsager reciprocity, and positivity of dissipation. For sufficiently simple systems this leaves only a few unknown coefficients in the Onsager matrix, which are taken as phenomenological parameters. The diagonal terms in the Onsager matrix are generalized diffusivities or relaxation rates, and have a familiar interpretation. In the present case, it turns out that the off-diagonal coupling between the concentration and strain variables is crucial to the physics. The size of this coupling could not be known from arguments as to the general form of the Langevin equations; more physical input is required. This leads to the second phenomenological approach, a two-fluid model of polymer and solvent [20,9,21,11,13].

In a two-fluid model of a polymer solution, the momentum densities of polymer and solvent are considered separately. That is, two separate equations are written to describe the evolution of the momentum densities of the polymer and solvent as a result of various stresses in the problem. Of course, only the total momentum density is a conserved quantity and thus a long-lived variable; if the polymer and solvent are moving relative to each other, large drag forces quickly make the two velocities equal. Nonetheless, it is useful to write separate momentum evolution equations, because certain stresses act directly on the polymer, while others act directly on the solvent and only influence the polymer through the large drag forces. This information turns out to determine the form of the coupling between polymer concentration and polymer elastic stress in the Langevin equation for concentration, as I shall show below.

Stresses acting on the polymer directly include the following.

(1) The polymer elastic stress $\Pi_{ij}^{(e)}$, which is communicated down the backbone of polymer chains. Under constant shear-flow conditions, this stress is continually built up by convection and slowly relaxed by repetition of entangled chains. This gives rise in steady state to large shear-rate-dependent stresses, i.e., large solution viscosities and/or normal stress coefficients.

(2) The osmotic stress $\Pi_{ij}^{(o)}=-\mu\delta_{ij}$, which is communicated by direct interactions between monomers. Gradients in the osmotic stress give rise to conventional polymer diffusion. The chemical potential is given generally by $\mu=\phi\delta F/\delta\phi-F/V$, where $F$ is the free energy and $V$ is the volume of the system. The free energy $F$ is the sum of a concentration-dependent modulus $E(\phi)$ times a function of the strain,

$$F^{(e)}=E(\phi)f_e(W)\ , \tag{1}$$

and an osmotic term

$$\begin{aligned}F^{(o)}(\phi)&=\int dx\left[f^{(o)}(\phi)+\tfrac{1}{2}(\nabla\phi)^2\right]\\&\approx\tfrac{1}{2}\int dq\,\chi^{-1}(q)|\phi(q)|^2\ .\end{aligned} \tag{2}$$

Here $\chi^{-1}(q)=(1+\xi^2q^2)\chi^{-1}$ is the inverse susceptibility, with $\chi^{-1}=\partial^2f^{(o)}/\partial\phi^2$.

(3) The drag force $\Gamma(\phi)(v_s-v_p)$ between solvent and monomer density, when the solvent and polymer velocities are not equal. This drag coefficient, by analogy to fluid flow through a porous medium [14], should be of order $\Gamma(\phi)\sim\eta_0/\xi_H(\phi)^2$, where $\eta_0$ is the solvent viscosity and $\xi_H$ is the hydrodynamic screening length [22].

Stresses acting on the solvent directly include the following.

(1) Solvent viscous stresses $\Pi_{ij}^{(s)}=\eta_0[\nabla_i(v_s)_j+\nabla_j(v_s)_i]$, which are negligibly small if the polymer solution is well entangled so that the solution viscosity is large compared to $\eta_0$.

(2) Hydrostatic pressure $-p\nabla_{ij}$, which enforces the constraint of the constant total density in an incompressible solution.

(3) The reaction couple of the drag force between solvent and monomer density.

The polymer concentration satisfies a conservation law with the polymer velocity $v_p$,

$$\dot\phi+\nabla\cdot\phi v_p=0\ . \tag{3}$$

Equations of motion for the solvent and polymer momentum densities $g_s=(1-\phi)\rho_s v_s$ and $g_p=\phi\rho_p v_p$ then take the form

$$\begin{aligned}0&=\dot g_p-\nabla\cdot(\Pi^{(o)}+\Pi^{(e)})-\Gamma(\phi)(v_s-v_p)\ ,\\0&=\dot g_s-\nabla\cdot\Pi^{(s)}+\nabla p+\Gamma(\phi)(v_s-v_p)\ .\end{aligned} \tag{4}$$

Equation (4) omits momentum convection, i.e., terms of the form $\nabla_i(\rho v_i v_j)$, because the Reynolds numbers of interest are very small.

The drag forces cancel in sum of the two momentum equations, which expresses conservation of the total momentum $g=g_p+g_s$:

$$0=\dot g+\nabla\mu-\nabla\cdot\Pi^{(e)}-\nabla\cdot\Pi^{(s)}+\nabla p\ . \tag{5}$$

The solution is assumed to be incompressible, which implies

$$0=\nabla\cdot g=\nabla\cdot[\rho_p\phi v_p+(1-\phi)\rho_s v_s]\approx\rho_s\nabla\cdot v_s \tag{6}$$

in the approximation that $\phi \ll 1$ and $\rho=\rho_p\phi+(1-\phi)\rho_s\approx\rho_s$.

Having written equations for two velocities, it is now fruitful to eliminate the polymer velocity in favor of the mass-averaged velocity. The two velocities are kept nearly equal by the action of the large drag forces; they differ slightly when the other stresses in Eq. (4) are nonzero. For the slow flows of interest, inertial terms may be neglected, which leads immediately to an expression for $v_p$ in terms of $v_s$:

$$v_p=v_s+\Gamma^{-1}(\nabla\cdot\Pi^{(o)}+\nabla\cdot\Pi^{(e)}) \ . \tag{7}$$

The polymer moves relative to the solvent as a result of gradients either in the osmotic or polymer elastic stress, with a small mobility determined by the ease of solvent flow through the polymer solution.

For dilute solutions, nearly all of the mass is solvent; that is, the solvent velocity and the mass-averaged velocity are equal to within terms of order $\phi$, which shall be neglected here.

Using Eq. (7) for $v_p$ in Eq. (3) for the polymer concentration gives the suggestive form

$$0=\dot{\phi}+\nabla\cdot v\phi+\nabla\cdot\zeta^{-1}(\nabla\cdot\Pi^{(o)}+\nabla\cdot\Pi^{(e)}) \ , \tag{8}$$

where $\phi\zeta\equiv\Gamma$. The term arising from the osmotic stress gradients is simply $\nabla\cdot(\zeta^{-1}\nabla\mu)$, which describes ordinary diffusion in response to chemical potential gradients. The physics of the two-fluid model is that the osmotic and elastic stress gradients appear in the same way in the diffusion equation for polymer concentration.

With the neglect of inertial terms and solvent viscous stresses, Eqs. (5) and (6) become

$$\begin{aligned}&\nabla\times(\nabla\cdot\Pi^{(e)})=0 \ ,\\ &\nabla\cdot v=0 \ .\end{aligned} \tag{9}$$

Equation (9) requires that the divergence of the polymer elastic stress tensor be the gradient of a scalar field. This constraint ultimately determines the perturbation of the velocity from the mean shear flow, as shown in Sec. III B. The physics here is the same as in conventional creeping-flow approximation of Newtonian liquids: if inertial terms are neglected, the velocity field is determined by the requirement that the viscous stresses be balanced by the pressure.

### D. Strain equation of motion

Since the polymer concentration is coupled to the polymer elastic stress, which relaxes slowly, an equation of motion must be supplied for the elastic stress itself. Again, I proceed phenomenologically. The ingredients for the equation of motion of some variable describing the polymer stress are as follows.

(1) Galilean invariance. The polymer stress is convected by the polymer velocity, because that velocity generates translations of the polymer. The convective terms are simplest written in terms of the polymer strain, however; this is because successive deformation tensors compose. The most convenient strain tensor for this purpose is [23]

$$\begin{aligned}&W=E\cdot E^T \ ,\\ &\delta r'=E\cdot\delta r \ .\end{aligned} \tag{10}$$

Here $E$ is the deformation tensor, which relates a displacement vector $\delta r'$ in a deformed state to $\delta r$ in the undeformed state. Successive deformations $E_1,E_2,\ldots,E_n$ give a total deformation tensor $E=E_n\cdot\cdots\cdot E_2\cdot E_1$.

The deformation tensor acting during a time $dt$ in an inhomogeneous velocity field is $E_{ij}=\delta_{ij}+(\partial v_i/\partial x_j)dt$, which leads to the convective part of the equation of motion for $W$,

$$\begin{aligned}&\dot{W}=-(v_p\cdot\nabla)W+L_p\cdot W+W\cdot L_p^T+\cdots \ ,\\ &(L_p)_{ij}=\nabla_j(v_p)_i \ .\end{aligned} \tag{11}$$

Here I have made the reasonable assumption that the polymer velocity convects the polymer strain tensor.

(2) Strain-free energy. The nonlinear relation between polymer elastic stress and strain is expressed in terms of the free energy functional of the strain $F^{(e)}$. Given such a functional $F^{(e)}$, the stress $\Pi^{(e)}$ is given generally by [23]

$$\Pi^{(e)}=2W\cdot\frac{\delta F^{(e)}}{\delta W} \ . \tag{12}$$

Because the stress-strain relation is nonlinear, the convective terms of Eq. (11) are cumbersome written in terms of the stress, which is why strain is chosen here as a dynamical variable. The stress attained by successive small shear deformations is not given by any simple composition law; straining an already strained polymer solution gives less additional stress—this is shear thinning.

(3) Exponential stress relaxation. It is a remarkable feature of the reptation theory of stress relaxation that stress in an entangled polymer solution relaxes with the same stress relaxation function $\psi(t)$, regardless of the amplitude or tensor character of the stress [15]. This occurs because the stress relaxes by the reptative diffusion of a polymer chain out of its distorted tube; the distorted tube bears the stress, but the rate at which the tube is forgotten is independent of the stress. The function $\psi(t)$ is approximately a single exponential [15]; for present purposes, the stress relaxes according to

$$\dot{\Pi}^{(e)}=\cdots-\tau^{-1}(\phi)\Pi^{(e)} \ . \tag{13}$$

Here and throughout this paper, the deviatoric stress, i.e., the stress minus its equilibrium isotropic value at the local concentration, has been used.

The relaxation term in the strain equation of motion is then determined by the chain rule,

$$\dot{W}_{ij}=\cdots-2\tau^{-1}\frac{\partial W_{ij}}{\partial\Pi^{(e)}_{kl}}W_{km}\frac{\delta F}{\delta W_{ml}} \ . \tag{14}$$

Combining these ingredients, the equation of motion for the polymer strain is

$$\dot{W} = -(v_p\cdot\nabla)W + L_p\cdot W + W\cdot L_p^T - 2\tau^{-1}\frac{\partial W}{\partial \Pi^{(e)}} : \left[ W\cdot\frac{\delta F}{\delta W}\right] , \qquad (15)$$

with the stress $\Pi^{(e)}$ given by Eq. (12), the polymer velocity $v_p$ given by Eq. (7), and the free-energy functional $F(W,\phi)$ yet to be specified.

### E. Canonical Langevin equations

The phenomenological equations of motion [Eqs. (8), (9), and (15)] for the polymer concentration, velocity, and polymer strain can be put in a more canonical form, as was first shown by Onuki. The canonical form for coupled Langevin equations, for which many important properties have been proven, is for a set of variables $\{\Psi_i\}$

$$\dot{\Psi}_i = (P_{ij}+\Gamma_{ij})\frac{\delta F}{\delta \Psi_j} = \eta_i , \qquad (16)$$

with $P_{ij}$ and $\Gamma_{ij}$ the Poisson-bracket and Onsager couplings, respectively. The Poisson-bracket couplings conserve free energy, while the Onsager couplings are dissipative. The Onsager matrix must satisfy the well-known reciprocity relation $\Gamma_{ij}=\Gamma_{ji}$. Equations of the form Eq. (16) have been shown to have positive energy dissipation, and to satisfy the fluctuation-dissipation theorem, when the Gaussian thermal-noise sources $\eta_i$ are chosen with the proper mean-square amplitudes:

$$\langle \eta_i(t)\eta_j(t')\rangle = 2\Gamma_{ij}\delta(t-t') . \qquad (17)$$

Consider first the polymer concentration equation (8). The stress terms driving the diffusion may be written in terms of thermodynamic derivatives; using the general relation $\mu=\phi\delta F/\delta\phi - F/V$ leads to an expression for $v_p$,

$$v_p = v + \Gamma^{-1}\left[ -\phi\nabla\frac{\delta F}{\delta\phi} - \nabla W : \frac{\delta F}{\delta W} + 2\nabla\cdot\left[ W\cdot\frac{\delta F}{\delta W}\right]\right] , \qquad (18)$$

and an equation of motion for $\phi$,

$$\dot{\phi} + \nabla\cdot v\phi + \nabla\cdot\zeta^{-1}\left[ -\phi\nabla\frac{\delta F}{\delta\phi} - \nabla W : \frac{\delta F}{\delta W} + 2\nabla\cdot\left[ W\cdot\frac{\delta F}{\delta W}\right]\right] = 0 . \qquad (19)$$

The conventional diffusion term $\nabla\cdot(\zeta^{-1}\phi\nabla\partial F/\partial\phi)$ is evidently a diagonal entry in the Onsager matrix; the couplings to the strain are off-diagonal Onsager entries. There must be corresponding terms in Eq. (15) for the strain. The corresponding terms are part of the convective terms in Eq. (15) in which a portion of $v_p$, namely, $-\Gamma^{-1}\phi\nabla\delta F/\delta\phi$, appears:

$$\dot{W}_{ki} = \left[\Gamma^{-1}\phi\nabla_j\frac{\delta F}{\delta\phi}\right]\nabla_j W_{ki} - \nabla_k\left[\Gamma^{-1}\phi\nabla_j\frac{\delta F}{\delta\phi}\right] W_{ji} + (\text{transpose}) + \cdots . \qquad (20)$$

The remaining pieces of $v_p$ contributing to convective terms in Eq. (15) involve only the strain itself, and can separately be put in an explicitly Onsager-symmetric form. Thus, if only Onsager symmetry is required, there is some ambiguity as to the choice of the convecting velocity for $W$ and hence the form of the equations of motion [Eqs. (8), (9), and (15)]. However, the physically reasonable assumption that the convective velocity for polymer strain is $v_p$ is consistent with Onsager symmetry.

The relaxational terms in Eq. (15), namely, Eq. (14), must likewise be shown to obey Onsager reciprocity. This is not manifest in the form of Eq. (14), and is most easily checked once a manageable form of $F(W)$ has been specified.

The velocity in the present theory is treated not as a fluctuating dynamical quantity, but only as a field satisfying the constraints of incompressibility and creeping flow, Eq. (9). Thus the appearances of velocity $v$ in the model equations are not quite of canonical Langevin form—there is no equation of motion for $v$. Nonetheless, the necessary properties can easily be demonstrated. First, note that the couplings of $\phi$ and $W$ to $v$ are evidently those mandated by Galilean invariance. Second, the convective terms involving the solution velocity $v$ can be shown to lead to positive dissipation, by considering the total derivative of the free energy:

$$\dot{F} = \int dx\frac{\delta F}{\delta\phi}\dot{\phi} + \int dx\frac{\delta F}{\delta W} : \dot{W} . \qquad (21)$$

Using the equations of motion (8) and (15) for $\phi$ and $W$ then gives

$$\dot{F} = -\int dx\, v\cdot\nabla F - \int dx\, v_j\nabla_l\Pi^{(e)}_{lj} . \qquad (22)$$

Now $\nabla\cdot v = 0$, so the first term vanishes; use of the Stokes equation (9) for $v$ converts the second term to $\eta_0\int dx(\nabla_i v_j)^2$. Thus the dissipation from the terms involving $v$ is indeed positive, and negligible if the solvent viscosity is to be neglected.

Finally, as the solvent viscosity is neglected, there is no need for random thermal forces acting on the total momentum density; the fluctuation-dissipation theorem relates the strength of thermal noise to the size of dissipative coefficients. Noise sources of canonical form may be added to Eqs. (8) and (15) to complete the Langevin equations.

### F. Role of $F(W)$

The final ingredient in the model formulation is an expression for the elastic free energy $F(W)$, from which the stress-strain relation is derived. The simplest such free energy is that which describes noninteracting Gaussian chains, which is appropriate for chains described by the Rouse model. As the Rouse model neglects both entanglement and hydrodynamic screening effects, this model is sensible only for polymer chains near the overlap concentration.

The Rouse form for $F(W)$ may be obtained by considering the partition function of a set of Gaussian chains with configurations $R(s)$ affinely distorted by a deformation tensor $E$:

$$Z=\int DR\,\exp\left[-\frac{3}{2a^2}\sum_{\alpha}\int ds\left[E\cdot\frac{\partial R^{\alpha}}{\partial s}\right]^2\right] . \tag{23}$$

The Gaussian integrals over the set of bond displacement variables may be evaluated to give a free energy

$$F^{(e)}(W)=\tfrac{3}{2}\int dV\,\phi\,\mathrm{tr}(W-\ln W) . \tag{24}$$

The corresponding stress-strain relation is linear:

$$\begin{aligned}&\Pi^{(e)}=E(\phi)(W-\delta) ,\\&E(\phi)=3\phi/a^2 .\end{aligned} \tag{25}$$

If the stress-strain relation is linear, then the strain as well as the stress relaxes with a time constant independent of strain. Indeed, using Eqs. (24) and (15) gives a strain equation of motion for a spatially uniform system under flow,

$$\dot{W}=L\cdot W+W\cdot L^{T}-\tau^{-1}(W-\delta) . \tag{26}$$

As discussed in the following section, the steady-state solution of this equation gives rise to a constitutive relation between the stress and the rate of strain tensor with viscosity and normal stress coefficients independent of shear rate. The model with the Rouse expression for $F(W)$ does not exhibit shear thinning. To obtain shear thinning, the stress-strain relation must be nonlinear, so that the relaxation time for the strain variable is not independent of strain.

Within the Doi-Edwards model of entangled polymer chains, nonlinearity in the stress-strain relation arises from the constraint of constant tube length. To see this, note that the general microscopic expression for the elastic stress tensor [15],

$$\Pi_{ij}^{(e)}(x)=(3/a^2)\sum_{\alpha}\int ds\,\delta(x-R^{\alpha}(s))\frac{\partial R_i^{\alpha}(s)}{\partial s}\frac{\partial R_j^{\alpha}(s)}{\partial s} , \tag{27}$$

may be interpreted as a sum of the contributions either from the literal microscopic bonds of the polymer chain, or from the segments of tube to which each polymer is confined. Doi and Edwards argue that the tube after an initial affine strain quickly recovers its equilibrium length, in a time short compared to the stress-relaxation time. If the tube length is constant, then from Eq. (27) the trace of the stress tensor should be constant.

Many models exist for $F(W)$ with the property that $\mathrm{tr}\Pi^{(e)}$ is constant, including for instance the independent alignment (IA) model. In the present approach, the IA model is not particularly convenient, because the stress-strain relation is not readily inverted. Thus the calculation of the relaxation term in the strain equation is problematic. Other more tractable phenomenological expressions for $F(W)$ exhibiting shear thinning exist; their consequences for polymer solutions in shear flow will be pursued in future work.

For present purposes of understanding the fluctuations of polymer solutions at low to moderate shear rates, it turns out that even the Rouse elastic energy is adequate for a qualitative description. Because of the other approximations made (retaining only strain as an additional variable, single stress-relaxation time), it is inappropriate to seek too accurate a form for $F(W)$.

## II. ADIABATIC APPROXIMATION

### A. Constitutive equation

Having derived an equation of motion for the polymer strain, I shall now review the adiabatic approximation, in which the time derivative of the strain is set to zero. This limit is valid for sufficiently long wavelengths and time scales such that the stress relaxes to a local equilibrium value. In other words, the adiabatic approximation holds when the solution is Newtonian. This section reviews the approach and results of Helfand and Fredrickson in Ref. [10].

As described after Eq. (26), the solution of the steady-state strain equation in a spatially uniform system gives a constitutive relation. For the simplest case of a Rouse solution under simple shear $\mathbf{v}=\dot{\gamma}y\hat{\mathbf{x}}$, the steady-state solution of Eq. (26) gives

$$\begin{aligned}&\Pi^{(e)}=\eta\dot{\gamma}(\hat{\mathbf{x}}\hat{\mathbf{y}}+\hat{\mathbf{y}}\hat{\mathbf{x}})+\psi_x\dot{\gamma}^2\hat{\mathbf{x}}\hat{\mathbf{x}} ,\\&\eta=G\tau , \quad \psi_x=2G\tau^2 .\end{aligned} \tag{28}$$

The Rouse constitutive relation is substituted into the equations for the polymer concentration [Eq. (8)] and velocity [Eq. (9)], and the result is expanded to linear order in deviations from the uniform concentration and shear flow. Here, I retain only terms to $O(\dot{\gamma})$ for simplicity. The result, first derived and explored by HF, is after Fourier transform

$$\begin{aligned}&\dot{\phi}+\dot{\gamma}q_x\frac{\partial\phi}{\partial q_y}+(Dq^2-2\dot{\gamma}\eta'\zeta^{-1}q_xq_y)\phi=\eta_{\phi} ,\\&D\equiv\zeta^{-1}\phi\frac{\delta F}{\delta\phi}\approx\zeta^{-1}\chi^{-1}\phi_0 .\end{aligned} \tag{29}$$

The perturbation of the velocity field from uniform shear flow is determined by the conditions (9). Substituting the constitutive relation and linearizing gives

$$\begin{aligned}&\delta\mathbf{v}=\frac{(q_y^2-q_x^2)\eta'}{q^3\eta}\dot{\gamma}\delta\phi\hat{\hat{\mathbf{q}}} ,\\&\hat{\hat{\mathbf{q}}}\equiv\hat{\mathbf{q}}\times\hat{\mathbf{z}} .\end{aligned} \tag{30}$$

At this level of approximation, the perturbation of the velocity field does not enter the concentration equation. The perturbation $\delta\mathbf{v}$ would enter the concentration equation through a term $\nabla_i[\nabla_j\eta(\nabla_i\delta v_j)]$; since $\delta\mathbf{v}$ is orthogonal to $\hat{\mathbf{q}}$, the contribution vanishes to linear order in $\delta\phi$.

### B. Effective diffusion constant

The terms driving polymer diffusion now have a form they may be summarized in terms of an anisotropic diffusion coefficient $D(\hat{\mathbf{q}})$, which at first order in shear rate is

$$D(\hat{\mathbf{q}})=D\left[1-2\dot{\gamma}\tau\frac{\partial\ln\eta}{\partial\ln\phi}\frac{G}{\chi^{-1}\phi_0^2}\hat{\mathbf{q}}_x\hat{\mathbf{q}}_y\right] . \tag{31}$$

In directions for which $D(\hat{\mathbf{q}})$ is smaller because of the shear-dependent terms, fluctuations decay more slowly. The amplitude of thermal noise generating the fluctuations is unaffected by shear, so an increased $S(q)$ should result in those directions. (This argument neglects the effects of the convective term $\dot{\gamma}q_x\partial\phi/\partial q_y$; the effects of this term are a recurring subject throughout this paper.) For the viscosity nonlinearity, the diffusion is most slowed along the line $q_x=q_y$; for the normal-stress nonlinearity, which contributes at higher shear rates, the diffusion is slowest for $q_y=0$.

From Eq. (31) a crude estimate of the size of the effect on $S(q)$ may be made. When $D(\hat{\mathbf{q}})$ is markedly anisotropic, or certainly when $D(\hat{\mathbf{q}})$ becomes negative in some directions, $S(q)$ will be strongly distorted. This occurs when

$$\dot{\gamma}\tau\frac{\partial\ln\eta}{\partial\ln\phi}\frac{G}{\chi^{-1}\phi_0^2}\approx 1 . \tag{32}$$

The effect of a given shear rate on $S(q)$ is evidently larger for long stress-relaxation times and large osmotic compressibilities. Hence well-entangled solutions relatively near a demixing transition should show strong effects of shear on $S(q)$.

### C. Fourier-space description

The linearized equation of motion (29) for the polymer concentration $\phi$ under the adiabatic approximation (28) may be solved for a given realization of the noise, and then averaged over the fluctuating noise with amplitudes given by the fluctuation-dissipation theorem. To motivate the solution, it is useful to describe the action of each of the terms in the Fourier-space equation of motion on a wave with wave vector $q$. Because the equation has been linearized, the fluctuating field may be built by superposition of such waves.

As discussed in the preceding section, the conventional diffusion term $Dq^2$ and the effects of the coupling to polymer elastic stress can be lumped into an effective $D(\hat{\mathbf{q}})$. The amplitude of a fluctuation at wave vector $q$ decays at a rate $D(\hat{\mathbf{q}})q^2$. The convective term $\dot{\gamma}q_x\partial\phi/\partial q_y$ has no effect on the amplitude of a fluctuation, but it changes the wave number of a fluctuation according to

$$\dot{\mathbf{q}}=-\dot{\gamma}q_x\hat{\mathbf{y}} . \tag{33}$$

That is, $\phi(\mathbf{q}(t))$ would be a solution of the equation of motion if the convective term were the only term acting on $\phi$. This flow in Fourier space is the Fourier transform of simple shear. With the diffusion active, the amplitude $a(q(t))$ of a wave initially at $q(0)$ evolves in time as

$$a(q(t))=\exp\left[-\int_0^t D(\hat{\mathbf{q}}(t'))q^2(t')dt'\right]a(q(0)) . \tag{34}$$

The thermal noise acts as a source of concentration fluctuations, which are then convected down the Fourier-space streamlines and decay by diffusion at the rate $D(\hat{\mathbf{q}})q^2$. An observer watching the concentration field at time $t=0$ at an observation wave vector $q_0$ would see contributions from fluctuations born "upstream" at times $t<0$ at wave vectors $q(t)$. Combining the results of Eqs. (33) and (34), the concentration at $q(0)=q_0$ and $t=0$ for a given realization of the noise is

$$\phi(q_0)=\int_{-\infty}^0 dt'\exp\left[-\int_{t'}^0 D(\hat{\mathbf{q}}(t''))q^2(t'')dt''\right] \times\eta_\phi(q(t')) , \tag{35}$$

which can be verified by substitution into Eq. (29).

The static structure factor $S(q)$ is given by the average over instances of the Gaussian random noise. The mean-square amplitude of the noise is given by Eq. (17); in the present case the Onsager coefficient is $\zeta^{-1}\phi_0$. Performing this average leads to an expression for $S(q)$ as presented by HF,

$$S(q_0)=\chi\int_{-\infty}^0 dt'\exp\left[-2\int_{t'}^0 D(\hat{\mathbf{q}}(t''))q^2(t'')dt''\right] \times[2Dq^2(t')] . \tag{36}$$

### D. No-convection limit

If the convective term $\dot{\gamma}q_x\partial\phi\,\partial q_y$ in Eq. (29) were not active, the solution for a given realization of the noise would not require a history integral. Then the structure factor would simply be

$$\begin{aligned}S(q)&=\chi D/D(\hat{\mathbf{q}})\\ &\approx\chi\left[1+2\dot{\gamma}\tau\frac{\partial\ln\eta}{\partial\ln\phi}\frac{G}{\chi^{-1}\phi_0^2}\hat{\mathbf{q}}_x\hat{\mathbf{q}}_y\right] .\end{aligned} \tag{37}$$

[In the absence of shear, the structure factor in the present model would be constant; a finite correlation length can be introduced simply by including gradient terms in the polymer free-energy density $f(\phi)$.]

In fact, Eq. (37) holds for sufficiently large wave numbers. For large $q$, the decay due to diffusion [assuming $D(\hat{\mathbf{q}})$ is everywhere positive] is so fast that the wave vector is convected a negligible amount by shear [Eq. (33)] during the lifetime of a fluctuation. The condition for Eq. (37) to hold is evidently

$$\dot{\gamma}\ll Dq^2 . \tag{38}$$

The first correction to the complete neglect of the convection at large $q$ may be found by treating the convective term in Eq. (29) as a perturbation. This leads to an additional contribution to the structure factor

$$\delta S(q)\approx\frac{\dot{\gamma}}{Dq^2}\hat{\mathbf{q}}_x\hat{\mathbf{q}}_y\frac{\partial\ln S(q)}{\partial\ln q^2}S(q) . \tag{39}$$

This first effect of affine convection reflects the affine distortion of a nonconstant $S(q)$. Notice that this term enhances scattering along the line $q_x=-q_y$, and suppresses fluctuations along $q_x = q_y$, i.e., the first and third quadrants of the shear plane in Fourier space. This is exactly the opposite of the effect of the term resulting from the concentration-dependent viscosity in Eq. (39). The convective term, present even in models of concentration fluctuations in mixtures of simple fluids, has a qualitatively different effect from the stress-induced discussion mechanism.

Another important feature of Eq. (39) is that the structure factor depends only on the direction $\hat{\mathbf{q}}$ in momentum space, and not on the magnitude of $q$; the enhanced scattering along $q_x = q_y$ persists at large $q$. This is not consistent with experimental observations, which find enhanced scattering only at sufficiently small wave numbers. The enhanced scattering at large $q$ is cut off by the breakdown of the adiabatic approximation, which I discuss in Sec. III.

### E. Enhanced fluctuations in real space

It is helpful to describe the origin of enhanced concentration fluctuations in real space, to gain some physical insight into the mechanism. I shall consider the simplest case within the adiabatic approximation of this section, namely, the growth arising from a concentration-dependent viscosity.

Consider a polymer solution in simple shear, with a circularly symmetric region temporarily containing more polymer than average because of a long-wavelength concentration fluctuation. The viscosity in this region is higher than in surrounding parts of the solution, because the concentration is higher, and $d\ln\eta/d\ln\phi > 0$. The velocity field is in general perturbed by the nonuniform viscosity; however, this is ignored in the discussion below, with the justification that the results of the discussion agree with the detailed calculations. The viscous stresses are then simply given by a constitutive relation for uniform shear, $\Pi^{(e)} = \eta(\phi)\dot{\gamma}(\hat{\mathbf{x}}\hat{\mathbf{y}} + \hat{\mathbf{y}}\hat{\mathbf{x}})$.

The viscous stresses are larger near the center of the concentrated region than in the surrounding solution. These stresses represent the pull of oriented polymer chains crossing a given surface dividing the polymer solution. One may envision the steps in the polymer chains as springs slightly oriented along the $q_x = q_y$ direction and giving rise to the stresses. Where there are more springs, or they are more oriented, the stresses are greater. The stresses acting on the boundaries of four subregions of the concentrated region, one in each quadrant, are represented by the arrows in Fig. 1. In a simple shear flow with uniform viscosity, the viscous stresses acting on the boundaries of a given region sum to zero. Because of the concentration-dependent viscosity, however, the viscous stresses acting a subregion in Fig. 1 do not sum to zero.

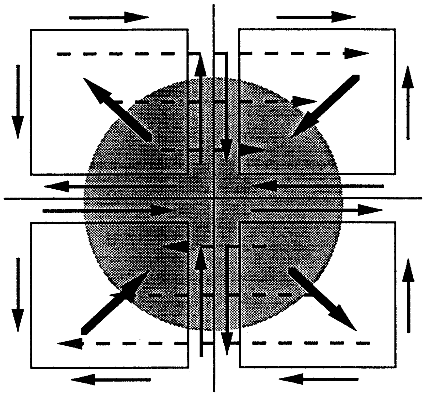

FIG. 1. Schematic illustration in real space of the polymer elastic stresses acting on a more-concentrated region (shaded). The simple shear flow is indicated by the dashed lines. The four regions of polymer bounded by squares have unbalanced elastic stresses acting on their boundaries. The stresses on each surface are shown as light solid arrows; the sum of elastic forces acting on each region are shown as heavy solid arrows.

There is a net elastic force acting on the polymer in the first and third quadrant pulling inwards towards the center of the dense region. Likewise there is an elastic force outwards, away from the center of the dense region, acting on the polymer in the second and fourth quadrants. These elastic forces are balanced by an equal and opposite drag force, arising from the flow of solvent relative to the polymer. In the first and third quadrants, the solvent must flow outwards as the polymer moves inwards, resulting in a drag force on the polymer directed outwards. In the second and fourth quadrants, the solvent flow and drag force on the polymer point inwards.

As a result, there is a tendency for a concentrated region to become narrower along the $q_x = q_y$ direction and broader in the orthogonal direction, exactly opposite to the effect of affine convection. The narrowing along the $q_x = q_y$ direction evidently opposes the broadening due to diffusion, leading to slower decay of concentration fluctuations modulated along that direction.

At the same time, of course, there are osmotic forces that tend to drive the polymer outward from the dense region, and cause inward solvent flow with a resulting equal and opposite drag force on the polymer, regardless of the direction in real space. In addition, the shape of the concentrated region would convect affinely in the absence of either this conventional diffusion or the stress-driven diffusion described above. The combination of these three processes determines the detailed evolution of the concentrated region.

## III. FLUCTUATIONS AND STRESS DYNAMICS

### A. Breakdown of adiabatic approximation

The adiabatic approximation assumes that the polymer elastic stress relaxes quickly to a value consistent with a steady state at a given local concentration and shear rate. That is, the adiabatic approximation assumes that the polymer elastic stress is given adequately by a constitutive relation between stress and shear rate. As shown in Sec. II D, this leads to a structure factor $S(q,\dot{\gamma})$ in shear that is larger in the first and third quadrants, in agreement with experiment. However, the resulting $S(q,\dot{\gamma})$ is only a function of $\hat{\mathbf{q}}$ for large $q$ until wave numbers so large that $q\xi \approx 1$, which does not agree with experiment.

The assumption that the stress relaxes quickly to a value given by the local steady state must break down when the time scale for the birth and death of concentration fluctuations becomes shorter than the stress-relaxation time. For wave numbers larger than a characteristic wave number $q^*$ such that

$$[D(q^*)]^2=\tau^{-1} , \tag{40}$$

the dynamics of the strain variable must become important. If the stress, responding with a finite response time $\tau$, is unable to follow the fast fluctuations of concentration at high wave numbers, then the mechanism for enhanced concentration fluctuations should become less effective than the adiabatic estimate. As a result, a theory that takes account of stress dynamics should predict a structure factor $S(q,\dot\gamma)$ that decreases for increasing $q>q^*$ down to $S(q,0)$.

For sufficiently small wave numbers, namely, the reverse of the condition (38), convection is important. For such wave numbers, the diffusive decay rate is so slow that the wave vector changes substantially by affine convection during the time it takes the fluctuation to decay. As a result, a fluctuation born in the regions of enhanced growth of fluctuations (i.e., $q_x=q_y$ for the viscosity nonlinearity) does not stay in that region long enough to be appreciably affected. The result of convection at small wave numbers is to make $S(q)$ smooth at the origin, eliminating the discontinuity implied by extrapolating Eq. (37) to $q=0$.

With stress-driven diffusion corresponding to a concentration-dependent viscosity only, there is no change in the decay rate of fluctuations along $q_x=0$. Thus if $S(q,\dot\gamma)$ is continuous at $q=0$, it must be that $S(0,\dot\gamma)=S(0,0)$ when only the concentration dependence of the viscosity is important. This, together with the enhanced growth of fluctuations for wave numbers $q<q^*$, should give rise to a peak in the structure factor with $q\approx q^*$ somewhere in the first and third quadrants, with a peak width of order $q^*$. This argument is confirmed by detailed calculations described below.

The presence of such a peak in $S(q,\dot\gamma)$ is in striking agreement with a series of light-scattering experiments of Pine and co-workers [2,24]. In their experiments, discussed further in Sec. IV, polymer solutions under moderate shear were observed to have enhanced light scattering with a broad peak in $S(q,\dot\gamma)$. The observed peak position corresponded to a length scale of fractions of a micrometer; the value of $q^*$ was in agreement with Eq. (40) and independently measured values of $D$ and $\tau$ from dynamic light-scattering and rheological measurements. All purely static lengths in the problem—the correlation length, the hydrodynamic screening length, the radius of gyration of the polymers—were at least an order of magnitude smaller than $(q^*)^{-1}$. The strikingly large length scale of the concentration fluctuations in these experiments arises from a comparison of time scales, namely, the stress-relaxation time and the diffusion rate.

### B. Minimal model

In Sec. I, coupled Langevin equation for concentration and polymer elastic strain were derived phenomenologically in some generality. In particular, the form of the elastic free energy was left unspecified, to allow for models with nonlinear stress-strain relations and shear thinning. Now, to illustrate in the simplest possible way the effects of stress dynamics on concentration fluctuations in polymer solutions under shear, I abandon that generality.

In principle, the equations [(8), (9), and (15)] with a shear-thinning $F(W)$ could be linearized about a state of uniform concentration and uniform shear flow at nonzero shear rate, and the linearized equations solved by a history integral similar to those of Sec. II C. Instead, I shall analyze in detail the model with $F(W)$ of Eq. (24) corresponding to Gaussian chains, for which there is no shear thinning, and only in the case of small shear rates. Two important simplifications entail: (1) the determination of the flow perturbation $\delta v$ is particularly simple, and (2) only a single component of the string tensor couples to the concentration. Thus a $5\times5$ set of equations coupling the $xx$, $yy$, and $zz$ components of the strain to the concentration, is reduced to a $2\times2$ set of equations. The results that follow are consistent with results obtained by Doi and Onuki [25] for the case of polymer-solvent mixtures.

In the particular case of the elastic free energy given by Eq. (24), the stress-strain relation $\Pi^{(e)}=G(W-\delta)$ is linear, and the relaxation term in Eq. (15) reduces to $\tau^{-1}(W-\delta)$. The concentration is to be expanded about $\phi=\phi_0$, the strain about $W_0=\delta+\tau(L_0+L_0^T)$ with $L_0=(\nabla v_0)^T$, and the velocity field about uniform shear $v_0=\dot\gamma y\hat{\mathbf{x}}$. The perturbations of concentration, strain, and velocity are denoted $\phi_1$, $W_1$, and $v_1$. The resulting expansion of Eqs. (8) and (15) gives

$$\begin{aligned} 0&=\dot W_1+v_0\cdot\nabla W_1-L_0W_1-W_1L_0^T-L_1W_0-W_0L_1^T\\ &\quad+\tau^{-1}W_1+\frac{\partial\tau^{-1}}{\partial\phi}\phi_1(W_0-\delta) ,\\ 0&=\dot\phi_1+v_0\cdot\nabla\phi_1+\phi_0\mathrm{tr}L_1 ,\\ (L_1)_{ij}&=\nabla_j(v_1)_i+\Gamma^{-1}\left[-\phi_0\chi^{-1}\nabla_i\nabla_j\phi_1\right.\\ &\qquad+\frac{\partial G}{\partial\phi}(W_0-\delta)_{ki}\nabla_j\nabla_k\phi_1\\ &\qquad\left.+G\nabla_j\nabla_k(W_1)_{ki}\right] . \end{aligned} \tag{41}$$

The dynamical analog of the HF mechanism—that the viscosity depends on concentration—appears in Eq. (41) in the form of concentration derivatives of $\tau(\phi)$ and $G(\phi)$. For instance, $W_1$ relaxes to a value $\phi_1W_0\partial(\ln\tau)/\partial\phi$ in response to a uniform concentration change $\phi_1$.

It turns out to be convenient to adopt a set of basis vectors $\{\hat{\mathbf{q}},\hat{\bar{\mathbf{q}}},\hat{\mathbf{z}}\}$ instead of $\{\hat{\mathbf{x}},\hat{\mathbf{y}},\hat{\mathbf{z}}\}$ for decomposing tensors such as the strain tensor and vectors such as the velocity perturbation $\delta v$. Here $\bar q=\hat{\mathbf{z}}\times q$ is a vector in the shear plane orthogonal to $q$; $\hat{\bar{\mathbf{q}}}$ is the corresponding unit vector. The affine convection of uniform shear flow means that $\hat{\mathbf{q}}$ is a function of time, which will be accounted for.

The incompressibility condition $\nabla\cdot v=0$ means that the velocity perturbation $v_1$ must be perpendicular to $q$, i.e., $\mathbf{v}_1 = i\hat{\hat{\mathbf{q}}}v_1$. The Stokes equation (9), when stresses due to solvent viscosity are neglected, implies that the divergence of the polymer elastic stress tensor must be the gradient of a scalar, so that it may be balanced by a pressure field. This implies

$$\begin{aligned} 0 &= \hat{\hat{\mathbf{q}}}_i \hat{\mathbf{q}}_j (\Pi^{(e)})_{ij} \\ &= \dot{\gamma}\tau G'(\hat{\hat{\mathbf{q}}}_x \hat{\mathbf{q}}_y + \hat{\hat{\mathbf{q}}}_y \hat{\mathbf{q}}_x)\phi_1 + G W_{q\bar{q}} , \end{aligned} \tag{42}$$

where $W_{q\bar{q}} \equiv \hat{\mathbf{q}} \cdot W_1 \cdot \hat{\hat{\mathbf{q}}}$. The vanishing of the $q\bar{q}$ component of the stress tensor is enforced in the equation of motion for the strain by choosing $v_1$ such that Eq. (42) is satisfied dynamically by the equation of motion for $W_{q\bar{q}}$.

The time derivatives of the components of $W$ have contributions from the components of $dW/dt$ and from the time dependence of $\hat{\mathbf{k}} = q$ and $\hat{\hat{\mathbf{q}}}$. For instance,

$$\partial_t W_{qq} = \hat{\mathbf{q}} \cdot \partial_t W \cdot \hat{\mathbf{q}} + \partial_t \hat{\mathbf{q}} \cdot W \cdot \hat{\mathbf{q}} + \hat{\mathbf{q}} \cdot W \cdot \partial_t \hat{\mathbf{q}} . \tag{43}$$

The equations of motion for the unit vectors $\hat{\mathbf{q}}$ and $\hat{\hat{\mathbf{q}}}$ are, from Eq. (33),

$$\partial_t \hat{\mathbf{q}} = \dot{\gamma} \hat{\mathbf{q}}_x (-\hat{\mathbf{y}} + q_y \hat{\mathbf{q}}) , \tag{44}$$

and $\partial_t \hat{\hat{\mathbf{q}}} = \hat{\mathbf{z}} \times \partial_t \hat{\mathbf{q}}$.

Using Eq. (43) with Eqs. (41) and (44) leads to equations of motion for $W_{qq}$ and $\phi$ that are decoupled from $W_{\bar{q}\bar{q}}$ and $W_{q\bar{q}}$ to $O(\dot{\gamma})$. Note that $v_1$ itself must be $O(\dot{\gamma})$ to satisfy the constraint equation (42), and the contribution of $v_1$ to $\dot{W}_{qq}$ through $\hat{\mathbf{q}} \cdot (L_1 \cdot W_0 + W_0 \cdot L_1^T) \cdot \hat{\mathbf{q}} \approx \hat{\mathbf{q}} \cdot (L_1 + L_1^T) \cdot \hat{\mathbf{q}}$ vanishes to $O(\dot{\gamma})$ because $\hat{\mathbf{q}} \cdot v_1 = 0$.

Thus the time dependence of $W_{qq}$ is unaffected by $v_1$ to $O(\dot{\gamma})$, and $v_1$ may be chosen to satisfy Eq. (41) with no effects on $W_{qq}$. Since only $W_{qq}$ appears in the concentration equation of motion, Eq. (41) has been reduced to a $2 \times 2$ system of equations. This simplification does not occur when terms of order $O(\dot{\gamma}^2)$ are retained.

The resulting pair of equations may be written in matrix form in terms of the two-component vector $\psi = (\phi/\phi_0, W_{qq})$:

$$\begin{aligned} &\dot{\psi} + \Omega \cdot \psi = \eta , \\ &\Omega = \begin{bmatrix} Dq^2(1 - 2r\alpha\dot{\gamma}\tau\hat{\mathbf{q}}_x\hat{\mathbf{q}}_y) & -Drq^2 \\ -2Dq^2(1 + 2\dot{\gamma}\tau\hat{\mathbf{q}}_x\hat{\mathbf{q}}_y) + 2(-\beta + 2\alpha r D q^2)\dot{\gamma}\tau\hat{\mathbf{q}}_x\hat{\mathbf{q}}_y & \tau^{-1} - 2\dot{\gamma}\hat{\mathbf{q}}_x\hat{\mathbf{q}}_y + 2Drq^2(1 + 2\dot{\gamma}\tau\hat{\mathbf{q}}_x\hat{\mathbf{q}}_y) \end{bmatrix} . \end{aligned} \tag{45}$$

Here $\alpha$, $\beta$, and $r$ are dimensionless constants, and $D$ is the mutual diffusion constant, given by

$$\alpha = \frac{\partial(\ln G)}{\partial(\ln\phi)} , \quad \beta = \frac{\partial(\ln\tau)}{\partial(\ln\phi)} , \quad r = G\chi , \quad D = \Gamma^{-1}\chi^{-1} , \quad \chi^{-1} = \phi_0^2 \frac{\partial^2 f}{\partial\phi^2} . \tag{46}$$

The corresponding Onsager and susceptibility matrices $\Gamma$ and $X^{-1}$ may be obtained by dropping all terms resulting from fluctuations of the Onsager coefficients themselves, multiplying the steady-state value of $\delta F/\delta W$. That is, the perturbation of the rate-of-strain tensor in Eq. (41) becomes [compare Eq. (18)]

$$(L_1)_{ij} = \nabla_j (v_1)_i + \Gamma^{-1} \left[ -\phi_0 \nabla_i \nabla_j \frac{\delta F}{\delta\phi} + 2(W_0)_{kl} \nabla_k \nabla_j \frac{\delta F}{\delta W_{li}} \right] . \tag{47}$$

The Onsager matrix is comprised of the resulting coefficients of $\delta F/\delta\phi$ and $\delta F/\delta W_{qq}$ in Eq. (41), written in the variables $\{\phi_1, (W_1)_{qq}\}$. The susceptibility matrix results from expanding the free energy $F(\phi, W)$ about the uniform steady state $\{\phi_0, W_0\}$ to second order in $\{\phi_1, W_1\}$. To $O(\dot{\gamma})$ the results are

$$\begin{aligned} \Gamma &= \begin{bmatrix} D\chi q^2 & -2D\chi q^2(1 + 2\dot{\gamma}\tau\hat{\mathbf{q}}_x\hat{\mathbf{q}}_y) \\ -2D\chi q^2(1 + 2\dot{\gamma}\tau\hat{\mathbf{q}}_x\hat{\mathbf{q}}_y) & 2/(G\tau)(1 + 2rD\tau q^2)(1 + 2\dot{\gamma}\tau\hat{\mathbf{q}}_x\hat{\mathbf{q}}_y) \end{bmatrix} , \\ X^{-1} &= \begin{bmatrix} \chi^{-1} & 0 \\ 0 & \frac{1}{2}G(1 - 2\dot{\gamma}\tau\hat{\mathbf{q}}_x\hat{\mathbf{q}}_y) \end{bmatrix} . \end{aligned} \tag{48}$$

The Onsager and susceptibility matrices here depend on the shear rate, because I have chosen to expand about a uniform steady state at nonzero shear. Note that Onsager symmetry has been preserved during the simplifications of this section. Noise sources have been restored to Eq. (45); their amplitudes are given by the relation Eq. (17).

### C. Without shear, a transient gel

Even in the absence of shear flow, the concentration and stress are dynamically coupled. Some of the consequences of this coupling were explored by Brochard and de Gennes, who introduced a simple model equivalent to Eq. (45) without shear ($\dot{\gamma} = 0$) on the basis of a two-fluid argument similar to that of Sec. I [9].

The basic physics of Eq. (45) without shear is that on time scales short compared to the stress relaxation time, the strain responds as if the solution were a gel, with a modulus equal to the plateau modulus. For instance, if a small droplet of concentrated polymer solution is immersed in pure solvent, the droplet may swell initially as solvent molecules invade the droplet before the chains in the droplet can disentangle.

The length scale below which this is an important effect is given by comparing the rate of solvent diffusion in the concentrated solution, $Dq^2$, with the stress relaxation time $\tau$. For droplets large compared to $(D\tau)^{1/2}$, a small skin on the surface swells as the chains on the surface of the droplet disentangle and diffuse into the solution. For a small droplet, the entire droplet swells as if it were a gel particle, until the stress relaxes. The crossover length scale, called the "magic length" by Brochard and de Gennes, is precisely the inverse of the characteristic wave number $q^*$ of Sec. II, which was determined by the same comparison of time scales.

Another important consequence of the dynamic coupling of concentration and strain is evident in the spectrum of fluctuations observed by dynamic light scattering (DLS). The relaxations of $\phi$ and $W_{qq}$ are coupled, so that the hydrodynamic modes do not have a simple dispersion relation. In the absence of the coupling, the eigenvalues of the matrix $\Omega(\dot{\gamma}=0)$ would be $Dq^2$ and $\tau^{-1}$; the diffusive mode would only involve the concentration, and the strain would relax independently. Because of the off-diagonal terms in the Onsager matrix, Eq. (48), the eigenmodes are "mixed" [26]. The matrix of response functions in a system of linear coupled Langevin equations is $R=(-i\omega\Gamma^{-1}+X^{-1})^{-1}$; the correlation function matrix is given by the fluctuation-dissipation theorem as $S=2(R+R^{\dagger})/\omega$. The concentration correlation function $S_{\phi\phi}(q,\omega)$ is measured in DLS. For the Onsager and susceptibility matrices of Eq. (48) at $\dot{\gamma}=0$, using the above expression for the matrix $S$, the correlation function $S_{\phi\phi}(q,\omega)$ is given by a weighted sum of two normalized Lorentzians:

$$S_{\phi\phi}(q,\omega)=\frac{2Dq^2}{r_2-r_1}\left[(\tau^{-1}/r_1-1)\frac{r_1/\pi}{\omega^2+r_1^2}+(1-\tau^{-1}/r_2)\frac{r_2/\pi}{\omega^2+r_2^2}\right] . \tag{49}$$

Here $r_1$ and $r_2$ $(r_1>r_2)$ are the two roots of the characteristic equation for $\Omega(\dot{\gamma}=0)$:

$$0=r^2-r(\tau^{-1}+Dq^2(1+2r))+Dq^2\tau^{-1} . \tag{50}$$

For small wave numbers, the roots approach $Dq^2$ and $\tau^{-1}+2rDq^2$. For larger wave numbers $q^*<q<\xi^{-1}$, the roots become $\tau^{-1}/(1+2r)$ and $Dq^2(1+2r)$; the crossover wave number then satisfies $Dq_c^2(1+2r)\approx\tau^{-1}$. Note that this is again the criterion for the characteristic wave number $q^*$, within the factor of order unity $1+2r$. A typical dispersion relation is shown in Fig. 2.

The relative weight of the two Lorentzians vanishes in the limit of small wave number—all of the weight is in the slowly relaxing diffusive mode. Thus in the true hydrodynamic limit, the stress is completely relaxed and the dynamic coupling is unimportant for concentration fluctuations. At large wave number, the ratio of the slowly relaxing to quickly relaxing Lorentzians becomes $2r$, and the slow and fast eigenvectors of the hydrodynamic matrix $\Omega$ are proportional to $(1,1/r)$ and $(1,-2)$, respectively. When $r$ is small, i.e., when the plateau modulus $G$ is much smaller than the osmotic modulus $\chi^{-1}$, the slow eigenvector is purely a strain relaxation, and the concentration fluctuations in DLS have mainly a fast component.

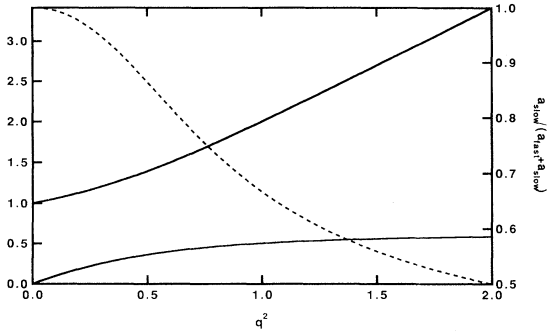

FIG. 2. The decay rates of the two coupled hydrodynamic modes in the two-fluid theory, plotted vs $q^2$, for $r=E\chi=0.25$. The dashed line shows the relative contribution of the slow mode to the concentration autocorrelation function.

### D. Large-$q$, no-convection limit

As discussed in Sec. II D, the effects of the affine-convection terms in the equations of motion may be neglected at large enough wave numbers such that Eq. (38) holds. Without these terms, the coupled equations (45) are easily solved for a given realization of the thermal noise without resort to a history integral. In the matrix notation, we have $\psi(t)=\int_{-\infty}^{t}dt'\exp[-(t-t')\Omega]\eta(t')$; the correlation function is $S_{ij}=\langle\psi_i(0)\psi_j(0)\rangle$. The average may be performed using Eq. (17) for the noise correlations to obtain the relation

$$\Omega\cdot S+S\cdot\Omega^T=2\Gamma . \tag{51}$$

To first order in shear rate, with $S=X+\delta S$ and $\Omega=\Omega_0+\delta\Omega$, one obtains

$$\Omega_0\cdot\delta S+\delta S\cdot\Omega_0^T=-(\delta\Omega\cdot X_0+X_0\cdot\delta\Omega) . \tag{52}$$

This relation [or indeed Eq. (51)] may be solved for $\delta S$ by regarding $\delta S$ as a three-component vector $(\delta S_{\phi\phi},\delta S_{\phi W},\delta S_{WW})$. The left-hand side may be represented as a linear operator and the corresponding matrix inverted. The result for the component $\delta S_{\phi\phi}$ to $O(\dot{\gamma})$ is

$$\delta S_{\phi\phi}=(\dot{\gamma}\tau)\chi(q)^2(r\alpha+(1+2rq^2)r\beta/\{1+q^2[\chi(q)^{-1}+2r]\})$$
$$\to\begin{cases}(\dot{\gamma}\tau)r(\alpha+\beta)\ , & q\to 0\\ (\dot{\gamma}\tau)r(\alpha+2r\beta/(1+2r))\ , & q^*\ll q\ll\xi^{-1}\\ (\dot{\gamma}\tau)r\alpha\chi(q)^2\ , & q\gg\xi^{-1} .\end{cases} \tag{53}$$

Observe that for $q > q^*$ and $r$ small, the effects of the concentration dependence of the stress-relaxation time, given by $\beta$, disappear; the stress-relaxation time is irrelevant on time scales such that the solution looks like a gel, and $r$ is small enough that the slow mode is purely strain relaxation. In this range of wave numbers, only the concentration dependence of the plateau modulus, given by $\alpha$, contributes to the growth of anisotropic fluctuations. This mechanism for producing "butterflies" in scattering from concentration fluctuations in strained gels has been discussed by several authors [27,28]. As $q$ becomes large enough that $\chi(q)^{-1} \neq 1$, even the contribution of $\alpha$ to concentration fluctuations is suppressed.

To summarize this behavior: neglecting effects of affine convection, (1) the structure factor should have a peak at $q^*$ because for wave vectors larger than this the growth of fluctuations due to dependence of $\tau$ on $\phi$ disappears; and (2) the high-$q$ shoulder of this peak should be rather broad, since not until $q \sim \xi^{-1}$ does the quiescent structure factor shut down the effects of the concentration-dependent modulus.

Evidently, Eq. (53) breaks down for sufficiently large $\dot{\gamma}$, since the change in $S(q)$ is no longer small. Note also that the argument that affine convection could be neglected was based on the assumption that the decay rate for fluctuations was essentially $Dq^2$; this certainly fails when the contributions of the stress-driven diffusion are of comparable order to $Dq^2$, which is the criterion for $\delta S(q,\dot{\gamma})$ of Eq. (51) to be of order $\chi(q)$ itself.

## IV. HISTORY-INTEGRAL SOLUTIONS

### A. Introduction

To obtain more complete information about the steady-state structure factor resulting from Eq. (45), a history-integral solution analogous to that of Sec. II C is necessary. Again, matrix notation is helpful. The set of equations (45) may be solved for a given realization of the thermal-noise vector by a time-ordered matrix-exponential history integral,

$$\psi(t)=\int_{-\infty}^{t} dt' M(t,t')\cdot\eta(q(t')) \,,$$
$$M(t,t')=T\left[\exp\left[-\int_{t'}^{t} dt''\Omega(q(t''))\right]\right] . \qquad (54)$$

The time-ordered exponential factor may be understood as an ordered product of exponentials of the hydrodynamic matrix at successive wave vectors on the affinely convected path leading from $q(t')$ for $t' < t$ to the observation wave vector $q(t)$:

$$M(t,t')=\lim_{\Delta\to 0}\exp[\Omega(q(t))\Delta]\cdot\exp[\Omega(q(t-\Delta))\Delta]\cdot\cdots\cdot\exp[\Omega(q(t'))\Delta] \,. \qquad (55)$$

Indeed, this is precisely how the expression may be evaluated numerically, as described below.

The matrix of correlation functions is evaluated by averaging the square of the vector $\psi(t)$ over the noise correlations using Eq. (17), with the result

$$S(q(t))=2\int_{-\infty}^{t} dt' M(t,t')\cdot\Gamma(q(t'))\cdot M^T(t,t') \,. \qquad (56)$$

Here $S(q)$ is computed at a wave vector $q(t)$, in which the time dependence represents the affine convection parallel to the $q_y$ axis.

I evaluate this expression by discretizing Fourier space along the $q_y$ axis, and so discretizing the history integral into a discrete number of events. If the variation of the convected wave number on the scale of the Fourier-space mesh is neglected, the following discrete evolution equation connecting $S(q(t))$ with $S(q(t-\Delta))$ can be derived:

$$\begin{aligned} S(t)&=2\left[\int_{t-\Delta}^{t} dt'+\int_{-\infty}^{t-\Delta} dt'\right] M(t,t')\cdot\Gamma(t')\cdot M^T(t,t') \\ &\approx\{A(t)-\exp[-\Delta\Omega(t)]\cdot A(t)\cdot\exp[-\Delta\Omega^T(t)]\} \\ &\quad+\exp[-\Delta\Omega(t)]\cdot S(t-\Delta)\cdot\exp[-\Delta\Omega^T(t)] \,, \end{aligned} \qquad (57)$$

with

$$2\Gamma(t)=\Omega(t)\cdot A(t)+A(t)\cdot\Omega^T(t) \,.$$

The first term $(t < t' < t-\Delta)$ represents the contribution of fluctuations born within the last time step; the second term $(t' < t-\Delta)$ represents the continuing decay of fluctuations born at some previous time step, at a wave vector "upstream" in the affine convection. When convection is unimportant, the exponential factors are large, the second term vanishes, and the equation reduces to $S=A$, or Eq. (51).

In practice, the computation of $S(q)$ begins with some large $q_y$, for which convective effects are unimportant and the mesh size is chosen small enough to give a reasonable representation of the $q$ dependence of $\Omega$ and $\Gamma$. Using Eq. (57), a single pass down a given axis in Fourier space parallel to the $q_y$ axis is sufficient to compute $S(q)$ all along that axis.

For the case of coupled equations, Eq. (45), the evolution equation (57) implies frequent evaluation of matrix exponentials. These may be efficiently calculated [29] by using the relation $\exp M=\lim_{n\to\infty}(\delta+M/n)^n$, where $\delta$ is the unit tensor. A value of $n=2^m$ is chosen sufficiently small based on some convenient norm of $M$ so that $\exp M \approx (\delta+M/n)^n$, and then $(\delta+M/n)$ is squared $m$ times. Typically $m$ is only logarithmic in the dimension $d_M$ of $M$, so this algorithm requires roughly $O(d_M^3 \ln d_M)$ scalar multiplications.

### B. Units and parameters

Before presenting the results of numerical calculations of $S(q,\dot{\gamma})$ based on Eq. (57), a system of appropriate units should be chosen, and the resulting dimensionless parameters identified. A natural choice of wave number and time scales in this problem are the characteristic wave number $q^*$ and the stress-relaxation time $\tau$.

The concentration variation may be measured in units of the mean concentration; the strain variable $W$ is, of course, dimensionless. Finally, since the system of equations are linear, each variable may be divided by $\chi^{1/2}$, to give $S_{\phi\phi}=1$ in absence of shear. The resulting forms of the hydrodynamic matrices are

$$\Omega=\Omega_0+\delta\Omega\ ,\quad \delta\Omega=\begin{bmatrix} -2\alpha r s\hat{q}_x\hat{q}_y & 0 \\ 2(-\beta+2\alpha r q^2)s\hat{q}_x\hat{q}_y & 0 \end{bmatrix},$$

$$\Omega_0=\Gamma X^{-1}\ ,\quad \Gamma=\begin{bmatrix} q^2 & -2q^2 \\ -2q^2 & 2/r(1+2rq^2) \end{bmatrix}, \tag{58}$$

$$X^{-1}=\begin{bmatrix} \chi^{-1} & 0 \\ 0 & r/2 \end{bmatrix}.$$

Here $s=\dot{\gamma}\tau$ is the dimensionless shear rate, and all appearances of $s$ other than those involving $\alpha$ and $\beta$ have been neglected for simplicity.

The dimensionless parameters in Eq. (58), defined in Eq. (46), are as follows.

(1) The logarithmic derivatives of the plateau modulus $E$ and stress-relaxation time $\tau$ with respect to concentration, denoted $\alpha$ and $\beta$. If these parameters are not of order unity, then large shear rates are needed before the stress-driven diffusion becomes important. Before such shear rates are reached, the small-shear rate expansion of Sec. III breaks down.

(2) The dimensionless ratio of plateau and osmotic moduli $r=G\chi$, which is a measure of the relative ease of dilating the transient gel and diluting the solution. If the solution is not easily compressed or is not well entangled, this parameter is small. Note that this parameter multiplies the terms in $\delta\Omega$; if $r$ becomes very small, the effect of shear on the concentration fluctuations becomes negligible because the polymer elastic stresses are small compared to the osmotic stresses.

(3) The dimensionless correlation length $\xi q^*$. As discussed in Sec. III D, a finite value of the correlation length is required to cut off the contributions of a concentration-dependent plateau modulus to the anisotropy in $S(q)$ for $q>q^*$.

The units and dimensionless parameters in the model may all be measured straightforwardly by rheology or dynamic light scattering. A measurement of the dynamic viscosity of the entangled solution determines the plateau modulus $G$ and the stress-relaxation time $\tau$; measurements as a function of concentration give $d\ln G/d\ln\phi$ and $d\ln\tau/d\ln\phi$. The mutual diffusion coefficient $D$ can be determined from DLS, and the osmotic compressibility $\chi^{-1}$ by some such probe as absolute-intensity static light scattering, or measurements of the osmotic pressure.

In short, with sufficient auxiliary measurements, there are no adjustable parameters in the present theory. In the absence of such measured values, the numerical results of the next section are presented for "typical" order-unity values of the two dimensionless parameters; specifically, $\xi q^*=0.15$, $r=0.25$, $\alpha=1$, and $\beta=4$, values which are comparable to those of the system reported in Refs. [2,3].

### C. Evolution of $S(q)$ with $\dot{\gamma}$

The main qualitative features of the static light-scattering measurements of Pine and co-workers [2,24] are reproduced by the numerical calculations, for reasonable values of the dimensionless parameters. These qualitative features are as follows.

(1) The structure factor indeed has a peak at $q$ of order $q^*$, with a peak width of the same order, as anticipated in the qualitative arguments of Sec. III A. A series of contour plots of the structure factor for increasing shear rate are displayed in Fig. 3.

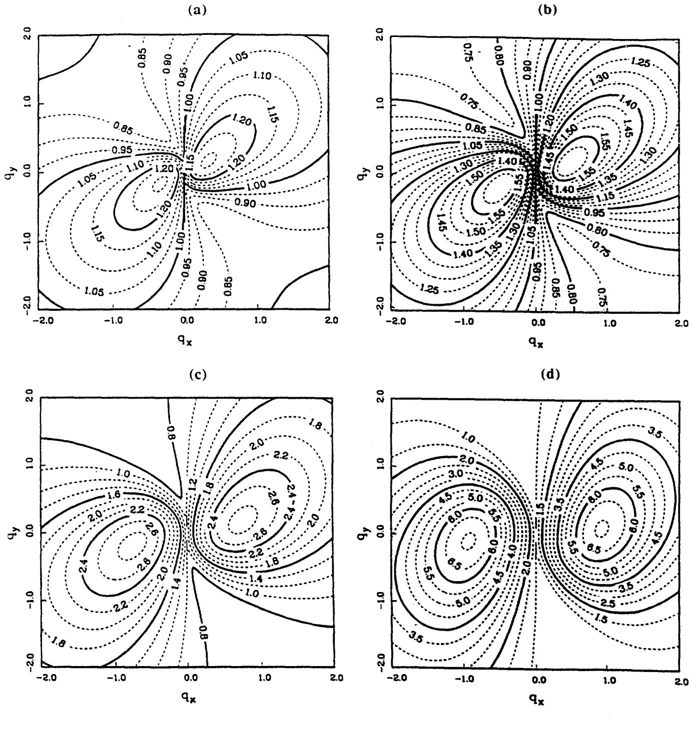

FIG. 3. Contour plots in the shear plane of the steady-state structure factor $S(q)$ for a sequence of increasing shear rates $\dot{\gamma}\tau=0.25, 0.5, 1, 2$. The wave numbers are given in units of $q^*$. Parameters for these plots are $\alpha=1$, $\beta=4$, $r=0.25$, and $\xi q^*=0.15$.

(2) The size of the peak in the structure factor grows with increasing shear rate. This may be measured in several ways: either the maximum intensity, or the total integrated intensity under the structure factor, may be plotted. (See Fig. 4.)

(3) The position of the peak at low shear is near the line $q_x = q_y$, i.e., 45° above the $q_x$ axis. As the shear rate is increased, the peak moves in the direction of affine convection in Fourier space. That is, the angle made by the peak wave vector with the $q_x$ axis decreases. (See Fig. 4.) The peak wave number is a rather weakly decreasing function of shear rate. (See Fig. 4.)

The explanations given in Sec. III A for the shape of the structure factor may be tested within the numerical calculation by artificially "turning off" various parts of the model. For instance, the action of the affine convection can be turned off artificially by replacing Eq. (57) with the limiting form Eq. (51) everywhere in Fourier space. At sufficiently small shear rates, the resulting structure factor is identical at sufficiently large wave number to the full model, but suffers a discontinuity at the origin, in which $\lim_{q\to 0} S(q)$ depends on the direction of approach. (See Fig. 5.) This is precisely the sort of dependence of $S(q)$ on $\hat{\mathbf{q}}$ of the no-convection limit discussed in Sec. III D. At larger shear rates, an eigenvalue of $\Omega$ becomes negative for a range of $\hat{\mathbf{q}}$ around the line $q_x = q_y$; then convection cannot be ignored for any wave number, since without convection the fluctuations would be unbounded for such $\hat{\mathbf{q}}$.

Next, the importance of the stress dynamics can be tested by evaluating the adiabatic approximation, Eq. (36), by numerical methods analogous to those presented in Sec. IV A. The resulting structure factor (see Fig. 6) is identical to the full model at sufficiently small wave number. For large $q$ the radial contour lines show the dependence of $S(q)$ only on $\hat{\mathbf{q}}$ described by HF. Here only $\xi^{-1} < \infty$ serves to cut off the increase in $S(q)$.

Finally, the origin of the dependence of peak position on shear rate may be explored, by computing a measure of the decay rate of fluctuations as a function of wave vector. The shifts of the peak location with increasing shear rate may be explained in two ways. First, at higher shear rate, the concentration dependence of the first normal-stress coefficient becomes important. This source of stress-driven diffusion has a different dependence on $\hat{\mathbf{q}}$. For the adiabatic approximation and the Rouse constitutive relation Eq. (28), diffusion driven by the first normal stress gives growth for $\hat{\mathbf{q}}$ along the velocity ($\hat{\mathbf{x}}$) direction, as discussed by HF. The normal-stress contributions are not accurately represented in the present calculations because of the expansion to first order in shear rate of Sec. III B.

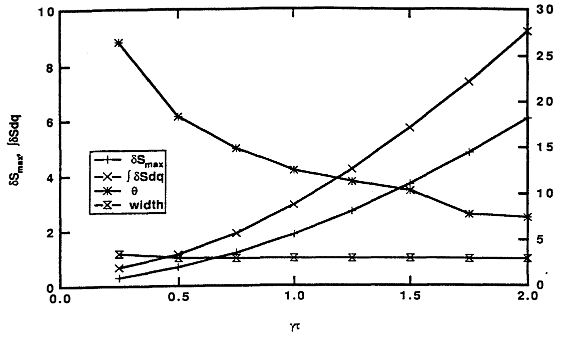

FIG. 4. Shown are shear-rate dependence of maximum (+) and integrated (×) intensity, peak width (X̄), and peak angle (∗). The intensity grows first linearly, then more strongly with shear rate; the peak width is roughly constant; the angle decreases with shear rate.

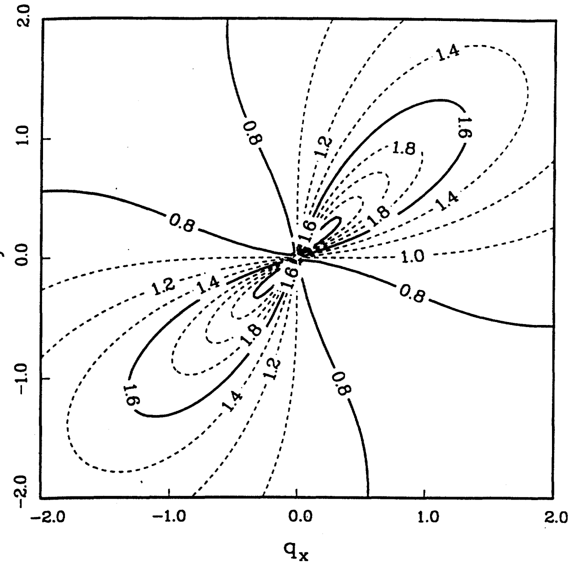

FIG. 5. Contour plots in the shear plane of $S(q)$ when the affine-convection term in the equation of motion is "turned off." Here $\dot{\gamma}\tau = 0.5$, with parameters as in Fig. 3. Note the discontinuity at the origin and the symmetry about the line $q_x = q_y$.

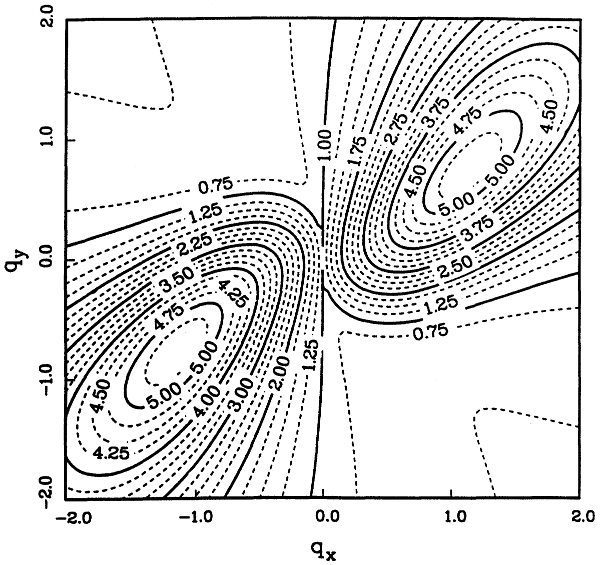

FIG. 6. Contour plots for the adiabatic approximation of Ref. [10] for shear rate $\dot{\gamma}\tau = 0.75$ and parameters as in Fig. 3. The peak is much larger than those of the complete theory; the peak is very broad in the direction of increasing wave number, cut off only by the nonzero correlation length $\xi$.

Second, the action of affine convection itself tends to move strong fluctuations from the region where they grow, along the "flow lines" in Fourier-transformed shear flow. Figure 5 shows that the structure factor with affine convection turned off is symmetric about the line $q_x = q_y$, while at the same shear rate the actual structure factor [Fig. 3(b)] already shows considerable shift of the peak away from this symmetry line. Hence the action of the convective terms is sufficient to produce the shifted peak position—though certainly at a higher shear rate, the normal-stress terms would begin to dominate.

### D. Transient effects

Experiments have also been carried out by Dixon, Pine, and Wu to study the time-dependent relaxation of the shear-induced scattering in entangled polymer solutions [3]. In these experiments, the steady-state structure factor is the initial condition, and the shear flow is stopped abruptly. Then, the time-dependent decay of the scattered intensity is observed at different wave vectors, and the relaxation rate is extracted.

It is found experimentally that the relaxation is well described by a single-exponential decay, in contrast to the DLS data on quiescent solutions. Furthermore, the relaxation rate as a function of wave vector agrees well with the lower of the two characteristic decay rates observed in DLS. Recall from Sec. III C that in DLS the relative amounts of slow- and fast-decaying signals are given by Eq. (49); at small $q$, all of the weight is in the slowly decaying signal, while at large $q$, the fast- and slow-decaying signals have comparable weight when the plateau and osmotic moduli are comparable.

This observation suggests that the shear flow is mainly stimulating the growth of the slowly decaying eigenmode of the hydrodynamic matrix, for large wave numbers. I now argue that this behavior suggests that the concentration dependence of the modulus, i.e., the parameter $\alpha$, is small. The correlation function itself can easily be shown to satisfy the following time-dependent equation when the shear flow is stopped:

$$\dot{S} + \Omega_0 \cdot S + S \cdot \Omega_0^T = 2\Gamma_0 \, , \tag{59}$$

which is solved by

$$\begin{gathered} S(t) = S_{\text{eq}} + \exp[-t\Omega_0] \cdot [S(0) - S_{\text{eq}}] \cdot \exp[-t\Omega_0] \, , \\ \Omega_0 \cdot S_{\text{eq}} + S_{\text{eq}} \cdot \Omega_0 = 2\Gamma_0 \, . \end{gathered} \tag{60}$$

Here the initial condition $S(0)$ is the steady-state value of $S$ under shear.

The initial condition $\tilde{S}(0) = S(0) - S_{\text{eq}}$ of $\tilde{S} \equiv S - S_{\text{eq}}$ may be expanded in the set of dyadics of eigenvectors of $\Omega_0$. If the $\tilde{S}(0)$ is composed of a dyadic of just the slowly relaxing eigenvector $\tilde{S}(0) = e_1 e_1^T$, then Eq. (60) implies that the relaxation of $\tilde{S}$ is single exponential.

The initial condition $\tilde{S}(0)$ solves the steady-state equation (51) for sufficiently large wave numbers and small shear rates that convection may be neglected. The expansion in dyadics corresponding to the $O(\dot{\gamma})$ result Eq. (53) is

$$\begin{aligned} \tilde{S} = {} & \frac{r\alpha s}{(1+2r)^2} [e_f e_f + 2r(e_f e_s + e_s e_f) + 4r^2 e_s e_s] \\ & + \frac{2r^2 \beta s}{1+2r} e_s e_s \, , \end{aligned} \tag{61}$$

where $e_f = (1, -2)$ and $e_s = (1, 1/r)$ are the fast and slow eigenvectors.

If $r\alpha \ll \beta$, or $r$ is large compared to unity, then only the dyadic $e_s e_s$ contributes appreciably to the sum, and the decay of $\tilde{S}$ will be approximately single exponential.

In the experiments of Refs. [2,3,24], comparison of the results of Sec. III C with DLS measurements give $r \approx 0.25$. Comparison of solvent viscosities and stress-relaxation times suggests that $\beta \approx 4$ and that $\alpha$ is small. The viscosity $\eta(\phi) \approx E(\phi)\tau(\phi)$ and the stress-relaxation time $\tau(\phi)$ are each increased by a factor of several hundred when the concentration is changed from the overlap concentration $\phi^*$ to about $5\phi^*$, so that almost all of the concentration dependence of $\eta$ is explained by an increased $\tau$.

## V. DISCUSSION

### A. Saturation effects

When the concentration fluctuations become large, linearization about the mean concentration is no longer a good approximation. Terms beyond the linearization of $\nabla\mu \approx \chi^{-1}\delta\phi$ enter to prevent large concentration fluctuations, as they must, since $\phi$ is a bounded variable.

The first nonlinear term in a simple theory to account for the suppression of large fluctuations is a correction to $\nabla\mu$ of order $\phi^3$, coming from a quartic term in the free-energy density $f^{(o)}(\phi)$. This leads to a nonlinear Langevin equation. A first approach to solving this equation would be to make a self-consistent mean-field approximation, replacing $\phi^3$ by $3\langle\phi^2\rangle\phi$, and computing the mean-square fluctuation $\langle\phi^2\rangle$ self-consistently. Qualitatively, this would lead to an effectively smaller osmotic compressibility as the concentration fluctuations became larger; thus the large growth of fluctuations reflected in Figs. 3 and 4 for large shear rates would be limited.

A rough criterion for the breakdown of the linearized theory compares the linear and nonlinear terms above; that is, the linearization fails when $\partial f/\partial\phi \sim \partial^3 f/\partial\phi^3 \langle\phi^2\rangle$. In a semidilute concentration range where $f$ is a power law in $\phi$, this gives the obvious condition $\langle\phi^2\rangle \sim \phi^2$. The mean-square fluctuation is given by the integral under $S(q)$; in the absence of shear this is roughly $\chi/a^3$, where $a$ is a microscopic cutoff. If the width of the shear-induced peak is of order $q^*$ in all directions, the integral under the peak is roughly $(q^*)^3 \chi S_{\text{max}}$. Hence the theory applies until $S_{\text{max}} \sim 1/(q^* a)^3$. Since $q^*$ is typically a small wave number, this is not a very restrictive condition. The concentration fluctuations induced by shear are large in spatial extent but small in amplitude.

### B. Shear thinning

The model formulation of Sec. I is sufficiently general to accommodate an elastic free energy corresponding to shear thinning, which becomes important in entangled solutions for shear rates greater than the stress-relaxation rate. A practical requirement is that the stress-strain relation must be invertible, since $\partial W/\partial \Pi$ is required to compute the Onsager coefficients in the strain equation of motion. This poses a problem for many common shear-thinning approximations, such as the independent-alignment model [15].

One tractable phenomenological expression for $F(W)$, for which the stress-strain relation may be given explicitly, is

$$\begin{aligned} F(W) &= G\ln[\operatorname{tr} W^{1/2}/(\det W)^{1/6}]\ , \\ \Pi &= G[W^{1/2}/(\operatorname{tr} W^{1/2}) - \delta/3]\ . \end{aligned} \tag{62}$$

This stress-strain relation (1) satisfies $\operatorname{tr}\Pi=\text{const}$, and (2) is in reasonable numerical agreement with the IA model for uniaxial strains, for which the IA stress may be simply computed.

In principle, as discussed in Sec. III B, a coupled set of linear Langevin equations could be obtained by expanding the full equations of motion, Eqs. (8), (9), and (15), about a state of uniform shear flow at a *finite* shear rate. The formally small quantity would be the concentration variation, and the deviation of the stress and velocity fields from their constant values would also be taken small. The simplifications of Sec. III B that resulted in a $2\times 2$ system of equations would be lost, but the numerical approach of Sec. IV would still be tractable, given the more complicated hydrodynamic matrix.

However, this program is of somewhat limited utility because of the dynamic instabilities that plague crude models of shear thinning. Typically, a model designed to preserve the "tube length" and thus the trace of the stress tensor has the feature that at some shear rate of a few times the stress-relaxation rate, the viscous stress falls with increasing shear rate. This leads to dynamic instabilities. Both the IA model and the elastic free energy of Eq. (62) have this property. Designing a suitable form for $F(W)$ without this pathology, and investigating its consequences in solutions under shear, is a subject for future work.

### C. Effect of normal stresses

At higher shear rates than those considered in Secs. III and IV, the effects of normal stresses become important. One effect of normal stresses, discussed in Sec. II B, was first analyzed by HF within the adiabatic approximation. That is, the directions in Fourier space in which decay of concentrations is slowed by normal-stress coupling are in the vicinity of $q_y=0$ for the Rouse constitutive relation, Eq. (28).

More generally, one may ask whether, at higher shear rates, the spinodal for demixing of the polymer and solvent is or is not shifted up or down in temperature. This paper has shown that the characteristic scattering peaks in polymer solutions under moderate shear are not caused by a shift in the spinodal, but that does not preclude shifts in the spinodal at higher shear.

Onuki has employed a natural criterion for the spinodal in a system under simple shear flow, namely, the instability of a concentration fluctuation with wave vector orthogonal to the velocity direction [17,30]. This criterion is natural, as well as convenient, because such a fluctuation is not distorted by the affine convection. In addition, one may consider a concentration fluctuation of sufficiently long wavelength that the stress-relaxation time is much shorter than the diffusion time. Then the adiabatic approximation of Sec. II is justified.

The most general constitutive equation consistent with the symmetry of simple shear is, to second order in shear rate,

$$\Pi^{(e)} = \eta\dot\gamma(\hat{\mathbf{x}}\hat{\mathbf{y}}+\hat{\mathbf{y}}\hat{\mathbf{x}}) + \dot\gamma^2(\psi_x\hat{\mathbf{x}}\hat{\mathbf{x}}+\psi_y\hat{\mathbf{y}}\hat{\mathbf{y}}+\psi_z\hat{\mathbf{z}}\hat{\mathbf{z}})\ . \tag{63}$$

with viscosity $\eta$ and normal-stress coefficients $\{\psi_\alpha\}$ functions of concentration.

Consider a concentration fluctuation $\delta\phi$ with wave vector along $\hat{\mathbf{y}}$. Equation (9), which determines the velocity perturbation for wave vector along $q_y$, implies simply that the shear stress is spatially constant; that is, the required velocity perturbation is a variation in the shear rate along the $y$ axis such that $\dot\gamma\eta=\text{const}$.

Using the constitutive relation (63) and the constant shear stress, Eq. (8) for the concentration with the adiabatic approximation becomes, to first order in $\delta\phi$,

$$\begin{aligned} 0 = {} & \dot\phi - D\partial_y^2\phi - \zeta^{-1}\partial_y^2((\alpha-1)F) \\ & + \zeta^{-1}(\eta\dot\gamma)^2\frac{\partial(\psi_y/\eta^2)}{\partial\phi}\partial_y^2\phi\ . \end{aligned} \tag{64}$$

The third term in Eq. (64), discussed by Onuki [30], is part of the chemical potential gradient $\nabla(\phi\partial F/\partial\phi - F)$. To second order in shear rate, this term may be replaced using a linear stress-strain relation $F(W)\approx(G/4)\operatorname{tr}(W-\delta)^2\approx(\eta\dot\gamma)^2/(2G)$.

The decay of fluctuations described by Eq. (64) may be summarized in terms of an effective diffusion coefficient $D_{\text{eff}}(\hat{\mathbf{q}})$, as in Sec. II B:

$$\begin{aligned} D_{\text{eff}}(\hat{\mathbf{q}}=\hat{\mathbf{y}}) = D + \zeta^{-1}(\eta\dot\gamma)^2 \Bigg[ & \frac{\alpha-1}{2}\frac{\partial(1/G)}{\partial\phi} \\ & - \frac{\partial(\psi_y/\eta^2)}{\partial\phi} \Bigg]\ . \end{aligned} \tag{65}$$

For wave vectors along the $\hat{\mathbf{z}}$ direction, there is no velocity perturbation needed to satisfy Eq. (9); then the shear rate is constant, but $\eta$ varies. The corresponding result for the effective diffusion coefficient is

$$D_{\text{eff}}(\hat{\mathbf{q}}=\hat{\mathbf{z}}) = D + \zeta^{-1}\dot\gamma^2\left[\frac{\alpha-1}{2}\frac{\partial(\eta^2/G)}{\partial\phi} - \frac{\partial\psi_z}{\partial\phi}\right]\ . \tag{66}$$

In each case, the terms proportional to $\alpha-1$ arise from the dependence of the chemical potential on the strain, as discussed by Onuki [30]. For the Rouse model, $G(\phi)\propto\phi$ and so $\alpha=1$, and these terms are absent, as found by HF.

The vanishing of $D_{\text{eff}}$ determines the spinodal. It is apparent that the location of the spinodal depends on the concentration dependences of $G$, $\eta$, and the normal-stress coefficients $\psi_y$ and $\psi_z$. It is not sufficient here to know the concentration dependence of the normal-stress differences. In the usual rheology of solutions of constant concentration or incompressible melts, the trace of the stress tensor is canceled by the pressure as the constraint of constant concentration or density is enforced.

Typically, the normal-stress coefficients scale as $\psi \sim G\tau^2$ and the viscosity scales as $\eta \sim G\tau$, so that $\psi/\eta^2 \sim 1/G$ and $\eta^2/G \sim \psi$; hence the two different derivative with respect to $\phi$ appearing in Eq. (65) [and likewise in Eq. (66)] are of the same magnitude. For rheological models in which the stress tensor has constant trace (signifying constant tube length; see Sec. I F), one obtains $\psi_x = 2N_1/3 + N_2/3$, $\psi_y = -N_1/3 + N_2/3$, and $\psi_z = -N_1/3 - 2N_2/3$, where $N_1$ and $N_2$ are the usual normal stress-difference coefficients. Hence $\psi_y$ and $\psi_z$ are both typically *negative*, since typically $N_1 > 2|N_2|$ and $N_2 < 0$.

Assuming $G$ and $\eta$ are increasing functions of $\phi$, and that $\psi_y$ and $\psi_z$ are negative and scale as described above, then both $O(\dot{\gamma}^2)$ terms lower $D_{\text{eff}}$ for $\hat{\mathbf{q}} = \hat{\mathbf{y}}$, and increase $D_{\text{eff}}$ for $\hat{\mathbf{q}} = \hat{\mathbf{z}}$. Hence the spinodal is shifted to higher temperatures for wave vectors along the gradient direction, and to lower temperatures for wave vectors along the vorticity direction, at second order in shear rate. The strain dependence of the chemical potential and the stress driven diffusion terms contribute with the same sign and comparable magnitudes to the spinodal shifts.

### D. Conclusions

This paper develops a dynamical description of coupled concentration fluctuations and stresses in an entangled polymer solution under shear. An essential ingredient of my approach is a two-fluid model of the polymer and solvent dynamics, similar to the approach of Brochard and de Gennes to fluctuations in quiescent semidilute polymer solutions. This approach leads naturally to stress-driven diffusion, i.e., a concentration current driven by an inhomogeneous elastic stress tensor, with the same mobility as the usual diffusion current driven by an inhomogeneous osmotic stress.

The resulting basic mechanism for enhanced concentration fluctuations in shear flow results from larger elastic stresses in regions of higher concentration. In a simple shear flow, the stresses act along $q_x = q_y$; consider a concentration fluctuation with wave vector in this direction. When the regions of higher concentration under higher stress try to collapse along $q_x = q_y$ to reduce their stress, the resulting force opposes conventional diffusion; such a fluctuation persists longer than in the quiescent state.

The previous work of Helfand and Fredrickson, in which an evolution equation for concentration was derived for chains obeying Rouse dynamics, analyzed the evolution of concentration fluctuations within an adiabatic approximation for the stress. That is, the stress was assumed to be given by a local constitutive relation. For sufficiently large wave numbers, the stress relaxation at a rate $\tau^{-1}$ cannot follow concentration fluctuations with diffusive decay rate $Dq^2$. Stress dynamics becomes important at $q^*$ such that $D(q^*)^2 \sim \tau^{-1}$, at which point the enhancement of concentration fluctuations becomes less effective than suggested by an adiabatic calculation. This leads to $q^*$ as a characteristic length scale for peaks observed in static light scattering of polymer solutions under shear.

The simplest theory of coupled concentration fluctuations and elastic stress results from an expansion to lowest order in shear rate, in which concentration fluctuations are coupled to a single component of the strain tensor. The resulting expression for $S(q)$ is a history integral over the birth and decay of fluctuation convected onto the observation wave vector. This expression may be effectively evaluated numerically. The resulting structure factor is in good qualitative agreement with static light scattering, with a broad peak at $q \sim q^*$, located for small shear along $q_x = \pm q_y$, and displaced for higher shear rates in the direction of affine convection in Fourier space.

The parameters in the theory, all experimentally accessible, are the ratio of elastic-to-osmotic moduli $G/\chi^{-1}$ and logarithmic derivatives with respect to concentration of $G$ and the stress-relaxation time $\tau$, as well as the dimensionless shear rate $\dot{\gamma}\tau$ and the length scale $q^*$. When $G/\chi^{-1}$ and the log derivatives of $G$ and $\tau$ are of order unity, strong effects of moderate shear $\dot{\gamma}\tau \sim O(1)$ on concentration fluctuations are expected.

The dynamical theory also provides a description of the relaxation of $S(q)$ from its steady state under shear to the quiescent equilibrium value. If the concentration-dependent stress relaxation time—which becomes irrelevant for $q > q^*$—is the dominant effect, then the relaxation to equilibrium takes place with a single exponential relaxation. This single relaxation time follows the lower branch of the two hydrodynamic modes of the two-fluid model; this behavior has been observed by Pine and co-workers [2,3,24].

At higher shear rates, it becomes essential to include normal stresses and shear thinning, both of which should arise from a more elaborate strain-free energy $F(W)$ and the same general coupled equations for the concentration fluctuations and elastic stress. To analyze experimental light-scattering results obtained in the flow-vorticity plane, $S(q)$ must be computed to at least $O(\dot{\gamma}^2)$ to see effects of normal stresses in the vorticity direction; this is a subject for future work.

Without computing the entire function $S(q)$ at larger shear rates, one can analyze the shift in the spinodal for concentration perturbations unaffected by the shear, i.e., with wave vectors normal to the flow. Shifts of the spinodal at $O(\dot{\gamma}^2)$ of comparable size and the same sign arise from the dependence of the chemical potential on strain, introduced by Onuki, and concentration dependence of normal-stress coefficients. In a solution with varying concentration, the actual normal stresses play a crucial role, as no constant-density constraint acts to cancel the isotropic elastic stress. In the gradient direction, the spinodal is found to be shifted to higher temperatures to $O(\dot{\gamma}^2)$, whereas in the vorticity direction the spinodal is suppressed.

## ACKNOWLEDGMENTS

I am pleased to thank Paul Dixon, Glenn Fredrickson, Gerry Fuller, Ron Larson, Dale Pearson, and Dave Pine for useful and enjoyable discussions.

[1] G. Ver Strate and W. Philippoff, Polym. Lett. **12**, 267 (1974); C. Rangel-Nafaile, A. B. Metzner, and K. F. Wissbrun, Macromolecules **17**, 1187 (1984), and references therein.

[2] X.-L. Wu, D. J. Pine, and P. K. Dixon, Phys. Rev. Lett. **66**, 2408 (1991).

[3] P. K. Dixon, D. J. Pine, and X.-L. Wu, Phys. Rev. Lett. **68**, 2239 (1992).

[4] T. Hashimoto, T. Takebe, and K. Fujioka, in *Dynamics and Patterns in Complex Fluids. New Aspects of the Physics-Chemistry Interface,* edited by Akira Onuki and Kyozi Kawasaki, Springer Proceedings in Physics Vol. 52 (Springer-Verlag, Berlin, 1990).

[5] T. Hashimoto and K. Fujioka, J. Phys. Soc. Jpn. **60**, 356 (1991).

[6] A. I. Nakatani, Y. Takahashi, and C. C. Han, Polymer Commun. **30**, 43 (1989).

[7] B. Hammouda, A. I. Nakatani, D. A. Waldow, and C. C. Han, Macromolecules **25**, 2903 (1992).

[8] M. Adam and M. Delsanti, Macromolecules **18**, 1760 (1985).

[9] F. Brochard and P.-G. de Gennes, Macromolecules **10**, 1157 (1977).

[10] E. Helfand and G. H. Fredrickson, Phys. Rev. Lett. **62**, 2468 (1989).

[11] M. Doi, in *Dynamics and Patterns in Complex Fluids: New Aspects of the Physics-Chemistry Interface* (Ref. [4]).

[12] A. Onuki, J. Phys. Soc. Jpn. **59**, 3427 (1990).

[13] S. T. Milner, Phys. Rev. Lett. **66**, 1477 (1991).

[14] M. A. Biot, J. Acoust. Soc. Am. **28**, 168 (1956); **28**, 179 (1956).

[15] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986), Chap. 7.

[16] D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry, and Correlation Functions* (Benjamin/Cummings, Reading, MA, 1978).

[17] A. Onuki, K. Yamazaki, and K. Kawasaki, Ann. Phys. **131**, 217 (1981), and references therein.

[18] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Ref. [15]), Chap. 4.

[19] K. Kawasaki and K. Sekimoto, Physica A **143**, 349 (1987).

[20] P.-G. de Gennes, Macromolecules **9**, 587 (1976); **9**, 594 (1976).

[21] F. Brochard, J. Phys. (Paris) **44**, 39 (1983).

[22] K. Freed and S. F. Edwards, J. Chem. Phys. **61**, 3626 (1974); P.-G. de Gennes, Macromolecules **9**, 594 (1976).

[23] R. G. Larson, *Constitutive Equations for Polymer Melts and Solutions* (Butterworths, Boston, 1988), Chap. 3.

[24] P. K. Dixon, D. J. Pine, and X.-L. Wu, Phys. Lett. **68**, 2239 (1992).

[25] M. Doi and A. Onuki, J. Phys. II (France) **2**, 1631 (1992).

[26] This is mathematically similar to the mixing of eigenstates by a perturbing potential in quantum mechanics; generically, the energy levels do not cross as a function of wave number.

[27] A. Onuki, J. Phys. II (Paris) **2**, 45 (1992); A. Onuki, J. Phys. Soc. Jpn. **58**, 3065 (1989).

[28] Y. Rabin and R. Bruinsma, Europhys. Lett. **20**, 79 (1992).

[29] C. Moler and C. Van Loan, SIAM Rev. **20**, 801 (1978).

[30] A. Onuki, Phys. Rev. Lett. **62**, 2472 (1989).