Langevin approach to polymers in flow

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A Gaussian polymer chain in simple shear flow is studied using Langevin equations. Incorporating hydrodynamic interactions to first order in $\epsilon \equiv 4-d$ (d is the spatial dimensionality) with the aid of field-theoretic methods, we solve these nonlinearly coupled kinetic equations for polymer-solvent dynamics and analytically evaluate the second normal stress coefficient Ψ_2 for small shear rates. It is found that the mean-field (consistent preaveraging) approximation for hydrodynamic interactions (HI) produces an unphysical positive Ψ_2, while inclusion of fluctuations in HI leads to a negative value for Ψ_2, in agreement with experimental evidence.

I. INTRODUCTION

Recent years have seen a great deal of research activities in polymer physics.[1-3] Many properties of polymers can now be understood from a theoretical point of view, ranging from equilibrium conformations of a single self-avoiding chain to reptation dynamics of polymer melts and to spinodal decomposition in polymer blends. Nevertheless, in spite of enormous efforts,[1-3] theories of the non-Newtonian flow characteristics are unsatisfactory and incomplete. This is because non-Newtonian phenomena involve strong flows and their adequate understanding requires sophisticated treatments of a highly nonequilibrium many-body system. The most widely used theory is that of Kramers[4] and Kirkwood,[4] based on the Kramers formula for polymer contributions to the total stress tensor and on the Kirkwood diffusion equation for polymer configurations. Many workers have applied this theory to study both linear and nonlinear viscoelasticity of polymers. For weak flows, Zimm[5] modeled a polymer chain with beads connected by massless springs and developed a successful theory of linear viscoelasticity by replacing the hydrodynamic interaction Oseen tensor with its *equilibrium* average. Pyun and Fixman[6] (PF) investigated fluctuations of the hydrodynamic interaction (HI) about its equilibrium average, in a subspace of eigenfunctions corresponding to the lowest excitations of the polymer normal modes. Bixon and Zwanzig[7] improved the PF results by performing calculations in a larger eigenspace. For strong flows, Peterlin[8] considered deformations of the polymer chain in flow to obtain an anisotropic steady state distribution for polymer conformations. Neglecting fluctuations in dealing with the HI, Fixman[9] also studied the non-Newtonian intrinsic viscosity. More recently, availability of large computers for the first time has allowed Ottinger[10] to adequately treat HI and to systematically evaluate rheological properties of polymers.

In all theoretical studies of polymer dynamics and hydrodynamics (rheology) of polymer solutions, the proper treatment of hydrodynamic interactions (HI) between polymer segments has presented a great challenge and led to severe mathematical complications, regardless of whether there is flow or not (i.e., in both linear and nonlinear response regimes). While recent field theoretic calculations of polymer properties have met some success in treating HI for zero[11] and weak[12] flows, similar calculations for rheological features in strong flows have not been reported. Since these modern field theoretic methods apply independently of the presence of any systematic flow, it should be possible, in principle, to perform such studies of non-Newtonian fluid dynamics of dilute polymer solutions.

Parallel to the dynamical theory of the Kirkwood diffusion equation, kinetic Langevin-type equations[13] for coupled polymer-solvent dynamics have recently been proposed in analogy to Onuki and Kawasaki's treatment[14] of critical dynamics of fluids under shear flow. Using these kinetic equations, several calculations have been made of the diffusion coefficient and dynamic chain correlation function in the absence of flow[15] and of dynamic mean-squared end-to-end distance of a Gaussian chain in weak homogeneous flows.[12] This Langevin approach, as opposed to the Fokker-Planck method (Kirkwood diffusion-equation approach), appears to be particularly useful for studying polymer dynamics and rheology involving strong linear and nonlinear flows. Here we adopt the Langevin description of polymer dynamics together with a Navier-Stokes Langevin equation for the solvent velocity field.[12,13,16]

We discuss the Langevin formulation and evaluation of the polymer stress tensor σ in as general a fashion as possible, specializing to particular examples only when further development can not proceed without detailed specifications. We consider directly the stress tensor σ because it is the central quantity in polymer rheology; for example, shear viscosity of dilute polymer solutions is related to the off-diagonal 12 component of σ (1 denoting the flow direction and 2 that of the velocity gradient). In this paper we evaluate the second normal stress Ψ_2 for small shear rates by performing lengthy calculations of the diagonal elements of σ. Hydrodynamic interactions are explicitly incorporated using the Gell-Mann–Low–type renormalization-group methods, in the limit

of dilute polymer solutions where dynamics of a single chain in flow plays a crucial role. Calculations of polymer properties–other than Ψ_2–such as viscosity, dynamic scattering factor, and radius of gyration in strong homogeneous flows, will be made in future studies. Those who are not interested in the details of the present calculation may skip to Sec. IV for discussions and summary.

This paper is organized as follows. In Sec. II, we first describe the kinetic Langevin-type equations for coupled polymer-solvent dynamics and formally solve these nonlinearly coupled dynamical equations by decomposition of polymer dynamics into drifting motion of the center of mass (c.m.) and internal dynamic motion of the chain relative to c.m. Then the Kramers-type formula for the stress tensor is derived in the present language. Explicit calculations for the stress tensor are carried out in Sec. III. In particular, we consider a simple shear flow and evaluate the stress tensor with and without the mean-field-type preaveraging approximation. In Sec. IV we discuss our results in the light of other previous calculations and present a brief summary of this work.

II. GENERAL FORMULATION AND SOLUTION

A. Coupled Langevin equations

Suppose that a homogeneous (laminar) flow

$$\mathbf{v}_0(\mathbf{r}) = \gamma \cdot \mathbf{r} \tag{2.1}$$

is applied to a dilute polymer solution at time $t = 0$, where the velocity gradient tensor γ is a traceless $d \times d$ unit matrix (d is the spatial dimensionality). The total velocity field in the polymer solution is then given by $\mathbf{u}(\mathbf{r},t) = \mathbf{v}_0(\mathbf{r}) + \mathbf{v}(\mathbf{r},t)$, where $\mathbf{v}(\mathbf{r},t)$ is the deviation from the unperturbed field $\mathbf{v}_0(\mathbf{r})$ due to the presence of polymers. The Fourier transform of the perturbation $\mathbf{v}(\mathbf{r},t)$ obeys the following Navier-Stokes Langevin equation[12,13,16]

$$\rho_0 \frac{\partial \mathbf{v}(\mathbf{k},t)}{\partial t} + \eta_0 k^2 \mathbf{v}(\mathbf{k},t) = T(\mathbf{k}) \cdot [\mathbf{F}(\mathbf{k},t) + \mathbf{f}(\mathbf{k},t)] , \tag{2.2}$$

where ρ_0 and η_0 are solvent density and viscosity, respectively. The transverse projection tensor

$$T(\mathbf{k}) = \mathbf{1} - \mathbf{k}\mathbf{k}/k^2 \tag{2.2a}$$

arises from use of the incompressibility condition to eliminate the hydrostatic pressure. $\mathbf{F}(\mathbf{k},t)$ is the Fourier transform of the polymer force density,

$$\mathbf{F}(\mathbf{k},t) = -\sum_{\alpha=1}^{N_p} \int_0^{N_0} d\tau_\alpha e^{-i\mathbf{k}\cdot\mathbf{c}_\alpha(\tau,t)} \frac{\delta H\{\mathbf{c}\}}{\delta \mathbf{c}_\alpha} . \tag{2.3}$$

H is the dimensionless Edwards Hamiltonian[17] for a polymer chain with configurations $\{\mathbf{c}\}$. The random force $\mathbf{f}$ is associated with solvent hydrodynamic fluctuations and therefore is present without polymers. Furthermore, we assume that $\mathbf{f}$ remains unaffected in presence of a small amount of polymers in dilution. We use here a standard continuum chain model for the polymers: $\mathbf{c}_\alpha(\tau,t)$ denote the position at time t of the polymer segment at the con-

tour point τ along the αth continuous chain (of length N_0). N_p is the total number of polymer chains in solution.

The single-chain dynamics is governed by a Langevin equation (omitting the subscript α)

$$\frac{\partial \mathbf{c}(\tau,t)}{\partial t} - \mathbf{v}_0(\mathbf{c}(\tau,t)) + \frac{1}{\zeta_0} \frac{\delta H\{\mathbf{c}\}}{\delta \mathbf{c}} = \mathbf{v}(\mathbf{c}(\tau,t),t) + \theta(\tau,t) , \tag{2.4}$$

where ζ_0 is the friction coefficient of a chain segment and $\theta(\tau,t)$ at τ is an uncorrelated random noise describing the Brownian motion of the segment τ. The random noises θ and $\mathbf{f}$ each have zero mean and their covariances are given by (in units where $k_B T = 1$)

$$\langle \theta(\tau,t)\theta(\tau',t') \rangle = (2/\zeta_0)\delta(\tau-\tau')\delta(t-t')\mathbf{1} , \tag{2.5a}$$

$$\langle \mathbf{f}(\mathbf{k},t)\mathbf{f}(\mathbf{k}',t') \rangle = 2\eta_0 k^2 \delta(\mathbf{k}+\mathbf{k}')\delta(t-t')\mathbf{1} , \tag{2.5b}$$

with $\mathbf{1}$ being the $d \times d$ unity matrix. Equations (2.2)–(2.4) are analogous to those employed to study critical fluids under shear flow[14] and have become a well established description of polymer dynamics.[12,13,15,16]

In writing (2.2) we have neglected the nonlinear fluid inertia term since the applied flow $\mathbf{v}_0$ is laminar and polymers are very small at hydrodynamic scales. For Gaussian chains the polymer force $\delta H\{\mathbf{c}\}/\delta\mathbf{c}$ can be modeled by harmonic springs so that it is linear in $\{\mathbf{c}(\tau,t)\}$. Then the left-hand side of each of (2.2) and (2.4) is linear in its own variable $\mathbf{v}(\mathbf{k},t)$ and $\mathbf{c}(\tau,t)$ respectively. However, due to the inhomogeneous terms on the right-hand side (RHS), Eqs. (2.2)–(2.4) are highly nonlinearly coupled, making exact solutions difficult to obtain.

B. Solutions to Eqs. (2.2)–(2.4)

Solution of (2.4) relies on obtaining the velocity perturbation $\mathbf{v}(\mathbf{x},t)$ near the polymer chain from the solution to (2.2). In the long-time limit (steady state), the fluid dynamics represented by the first term of (2.2) can be ignored, i.e., the Markovian approximation is legitimate.[18] The real space solution to Eq. (2.2) is first derived through inverse Fourier transformation

$$\mathbf{v}(\mathbf{c}(\tau,t),t) = \int_{\mathbf{k}} (\eta_0 k^2)^{-1} T(\mathbf{k}) \cdot [\mathbf{f}_{\mathbf{k}}(t) + \mathbf{F}(\mathbf{k},t)] e^{i\mathbf{k}\cdot\mathbf{c}(\tau,t)}$$
$$= \mathbf{v}_f(\mathbf{c}(\tau,t),t) + \mathbf{v}_F(\mathbf{c}(\tau,t),t) , \tag{2.6}$$

where $\int_{\mathbf{k}} = (2\pi)^{-d} \int d^d k$ in d dimensions and $\mathbf{v}_f$ and $\mathbf{v}_F$ denote the contributions from the random force $\mathbf{f}_{\mathbf{k}}(t)$ and $\mathbf{F}(\mathbf{k},t)$ respectively.

Polymer dynamics involves the internal motion of a polymer chain and the drifting motion of its center of mass. In the present study the internal dynamics plays the crucial role. Therefore we decompose the polymer motion into that of the center of mass $\mathbf{R}_{c.m.}(t)$ and relative motion $\mathbf{R}(\tau,t)$, namely, $\mathbf{c}(\tau,t) = \mathbf{R}_{c.m.}(t) + \mathbf{R}(\tau,t)$. Denoting the c.m. velocity by $\mathbf{v}_{c.m.}(t) = \partial\mathbf{R}_{c.m.}(t)/\partial t$, we transform (2.4) to a dynamic equation for polymer *internal* motion

$$\frac{\partial \mathbf{R}(\tau,t)}{\partial t} - \gamma \cdot \mathbf{R}(\tau,t) + \frac{1}{\zeta_0} \frac{\delta H\{\mathbf{R}\}}{\delta \mathbf{R}}$$

$$= [\mathbf{v}_0(\mathbf{R}_{c.m.}(t)) - \mathbf{v}_{c.m.}(t)] + \mathbf{v}(\mathbf{R}_{c.m.}(t) + \mathbf{R}(\tau,t), t)$$

$$+ \boldsymbol{\theta}(\tau,t) , \tag{2.7}$$

where use is made of (2.1). The first term on the RHS of (2.7) is independent of the contour variable τ and is denoted below as $\mathbf{v}^0(t)$.

The Edwards Hamiltonian H is given by

$$H\{\mathbf{R}(\tau,t)\} = \frac{1}{2} \int_0^{N_0} d\tau \left| \frac{\partial \mathbf{R}(\tau,t)}{\partial \tau} \right|^2$$

$$+ (v_2^0/2) \int_0^{N_0} d\tau \int_0^{N_0} d\tau' \delta(\mathbf{R}(\tau,t)$$

$$- \mathbf{R}(\tau',t)) , \tag{2.8}$$

where v_2^0 is the two-body excluded volume parameter and δ is a Dirac delta function. The first term is the elastic (entropic) free energy of a harmonic spring, corresponding to a Gaussian backbone in a chain. The second represents repulsive excluded volume interactions between different portions of the chain. The polymer force in (2.7) thus consists of two parts, a linear spring force and a repulsive one due to excluded volume interactions

$$\frac{\delta H\{\mathbf{R}(\tau,t)\}}{\delta \mathbf{R}(\tau,t)} = -\frac{\partial^2 \mathbf{R}(\tau,t)}{\partial \tau^2} + v_2^0 \nabla \rho(\mathbf{x},t)|_{\mathbf{x}=\mathbf{R}(\tau,t)} . \tag{2.9}$$

Here the second term has been expressed in terms of the monomer number density $\rho(\mathbf{x},t)$ of a single chain, defined as $\rho(\mathbf{x},t) = \int_0^{N_0} d\tau \, \delta(\mathbf{x} - \mathbf{R}(\tau,t))$.

Inserting (2.9) into (2.7) allows the Langevin equation (2.7) to be formally solved in term of its Green's function G_0 as

$$\mathbf{R}(\tau,t) = \mathbf{R}_0(\tau,t) + \mathbf{R}_F(\tau,t) + \mathbf{R}_f(\tau,t) + \mathbf{R}_{excl}(\tau,t) . \tag{2.10}$$

The leading order solution—i.e., that which would obtain in the absence of hydrodynamic and excluded volume interactions—is given by

$$\mathbf{R}_0(\tau,t) = \int_0^t dt' P(t-t') \cdot \mathbf{v}^0(t')$$

$$+ \int_0^{N_0} d\tau' G_0(\tau\tau'|t) P(t) \cdot \mathbf{R}(\tau')$$

$$+ \int_0^{N_0} \int_0^t d\tau' dt' G_0(\tau\tau'|t-t')$$

$$\times P(t-t') \cdot \boldsymbol{\theta}(\tau',t') . \tag{2.10a}$$

Here the flow propagator P is a matrix, defined by

$$P(t) = e^{\gamma t} \tag{2.10b}$$

and G_0 is found to have the form

$$G_0(\tau\tau'|t) = (2/N_0) \sum_{p=1}^{\infty} \cos(\hat{p}\tau) \cos(\hat{p}\tau') e^{-\lambda_p t} , \tag{2.10c}$$

with the relaxation rate λ_p given by

$$\lambda_p = \hat{p}^2/\zeta_0, \quad \hat{p} = \pi p/N_0 . \tag{2.10d}$$

For the evaluation of polymer stress tensor, the first term

of (2.10a) does not enter into the actual calculation; its second term involves the initial polymer configurations $\{\mathbf{R}(\tau)\}$ and therefore also becomes irrelevant in the long-time steady-state limit. Thus only the third term in (2.10a) contributes to σ.

The correction terms due to the velocity perturbation $\mathbf{v}$ (i.e., hydrodynamic interactions) and excluded volume interactions are similarly determined to be

$$\mathbf{R}_F(\tau,t) = \int_0^{N_0} \int_0^t d\tau' dt' G_0(\tau\tau'|t-t') P(t-t')$$

$$\cdot \mathbf{v}_F(\mathbf{R}(\tau',t'),t') , \tag{2.10e}$$

$$\mathbf{R}_f(\tau,t) = \int_0^{N_0} \int_0^t d\tau' dt' G_0(\tau\tau'|t-t') P(t-t')$$

$$\cdot \mathbf{v}_f(\mathbf{R}_{c.m.}(t') + \mathbf{R}(\tau',t'),t') , \tag{2.10f}$$

and

$$\mathbf{R}_{excl}(\tau,t) = -\int_0^{N_0} \int_0^d d\tau' dt' G_0(\tau\tau'|t-t') P(t-t')$$

$$\cdot (v_2^0/\zeta_0)$$

$$\times \nabla \rho(\mathbf{x}',t')|_{\mathbf{x}'=\mathbf{R}(\tau',t')} . \tag{2.10g}$$

where $\mathbf{v}_F$ and $\mathbf{v}_f$ have been defined by (2.6)

C. Kramers formula

In order to obtain an expression for polymer contributions to the stress tensor, let us consider the small wave number limit of (2.2) and (2.3). The magnitude of the relative coordinate $\mathbf{R}_\alpha$ is at most as large as the polymer size R_G (radius of gyration); thus at hydrodynamic scales (small $|\mathbf{k}|R_G$) the factor $e^{-i\mathbf{k}\cdot\mathbf{R}_\alpha(\tau,t)}$ can be expanded to leading order in $\mathbf{k}\cdot\mathbf{R}_\alpha$ and the expression (2.3) becomes

$$\mathbf{F}(\mathbf{k},t) = \sum_{\alpha=1}^{N_p} \int_0^{N_0} d\tau_\alpha i\mathbf{k}\cdot\mathbf{R}_\alpha(\tau,t) \frac{\delta H\{\mathbf{R}_\alpha\}}{\delta\mathbf{R}(\tau_\alpha,t)} e^{-i\mathbf{k}\cdot\mathbf{R}_{c.m.\alpha}} . \tag{2.11}$$

where use is made of the fact that the total intramolecular forces sum up to zero. Now the stress tensor σ can be identified through the relation $\mathbf{F}(\mathbf{k},t) = -i\mathbf{k}\cdot\sigma_\mathbf{k}$. Comparing with (2.11), we obtain σ in real space

$$\sigma = -\sum_{\alpha=1}^{N_p} \delta(\mathbf{r}-\mathbf{R}_{c.m.\alpha}) \int_0^{N_0} d\tau_\alpha \mathbf{R}_\alpha(\tau,t) \frac{\delta H\{\mathbf{R}_\alpha\}}{\delta\mathbf{R}(\tau_\alpha,t)} . \tag{2.12}$$

Consideration of a dilute solution of polymer chains with a uniform distribution allows us to neglect interactions between different polymer chains. In this dilution limit the dynamics $\mathbf{R}_\alpha(\tau,t)$ of the αth chain does not depend on the motion of others. Thus averaging (2.12) over Gaussian random forces $\{\boldsymbol{\theta}(\tau,t)\}$ and $\mathbf{f}(\mathbf{r},t)$ and over the uniform distribution of polymers, and taking the long-time limit, we derive the final expression for the steady-state polymer stress tensor

$$\sigma_{Langevin} = -n_p \lim_{t\to\infty} \int_0^{N_0} d\tau \left\langle \mathbf{R}(\tau,t) \frac{\delta H\{\mathbf{R}(\tau,t)\}}{\delta\mathbf{R}(\tau,t)} \right\rangle_{\theta,f} , \tag{2.13}$$

where $n_p = N_p / V$ is the polymer number density. Notice that (2.13) is identical *in form* to the Kramers formula[2-4] for the stress tensor in the Kirkwood-Kramers theory.

III. EVALUATION OF STRESS TENSOR

A. First-order solution

The polymer dynamics, in terms of the dynamic position variable $R(\tau, t)$, has been treated here without approximations by the nonlinear integral equation (2.10) with (2.10a)–(2.10g). If the integral kernel is small this nonlinear integral equation for $R(\tau, t)$ permits a perturbative solution. Our observation is that $R_0(\tau, t)$ is the leading-order term in the integral equation and that the other terms in (2.10) are small corrections[13] of order $O(\epsilon)$

in higher dimensions than 3, i.e., in $d = 4 - \epsilon$. Namely, $R_F(\tau, t)$, $R_f(\tau, t)$ and $R_{excl}(\tau, t)$ are small when $\epsilon = 4 - d \rightarrow 0$. The reason for the smallness (in $d \approx 4$ dimensions) of excluded volume and hydrodynamic interactions among a polymer chain is that the fractional dimensionality (which is 2 for a Gaussian chain) of a polymer is very low at *four* dimensions (roughly equivalent to a line of measure zero in three dimensions) and interactions rarely occur between different parts of such a low dimension polymer. So it is justified to perform perturbation calculations for hydrodynamic and excluded volume interactions at a high dimensionality $d = 4 - \epsilon$, near 4 and expand in the small parameter ϵ. Below we employ this widely applied ϵ-expansion technique and perform calculations to first order in ϵ. Thus $O(\epsilon)$ corrections to the zero-order polymer dynamics $R_0(\tau, t)$ of (2.10a) are obtained by iterating (2.10) a single time,

$$R_{1F}(\tau, t) = \int_0^{N_0} \int_0^t d\tau' dt' G_o(\tau\tau' | t - t') P(t - t') \cdot v_F[R_0(\tau', t'), t'] , \tag{2.10e'}$$

$$R_{1f}(\tau, t) = \int_0^{N_0} \int_0^t d\tau' dt' G_0(\tau\tau' | t - t') P(t - t') \cdot v_f[R_{c.m.}(t') + R_0(\tau', t'), t'] , \tag{2.10f'}$$

$$R_{1\,excl}(\tau, t) = - \int_0^{N_0} \int_0^t d\tau' dt' G_0(\tau\tau' | t - t') P(t - t') \cdot (v_2^0 / \zeta_0) \nabla \rho(x', t')|_{x' = R_0(\tau', t')} , \tag{2.10g'}$$

where the subscript 1 denotes the fact that (2.10e')–(2.10g') are *first*-order corrections. In terms of Eqs. (2.6) and (2.10a), the first-order solutions (2.10e')–(2.10g') are completely specified. Now we are ready to evaluate the stress tensor to $O(\epsilon)$ through the derived expressions (2.13), (2.10a), and (2.10e')–(2.10g'). From now on we consider Gaussian chains only, deferring calculations with excluded volume interactions to future work. So we drop $R_{excl}(\tau, t)$ in (2.10), keep only the first term in (2.9), and introduce the following quantities for notational simplicity:

$$Q_0(\tau, t) = \left\langle R_0(\tau, t) \frac{\partial^2 R_0(\tau, t)}{\partial \tau^2} \right\rangle_{\theta, f} , \tag{3.1a}$$

$$Q_{ff}(\tau, t) = \left\langle R_{1f}(\tau, t) \frac{\partial^2 R_{1f}(\tau, t)}{\partial \tau^2} \right\rangle_{\theta, f} , \tag{3.1b}$$

$$Q_{10}(\tau, t) = \left\langle R_{1F}(\tau, t) \frac{\partial^2 R_0(\tau, t)}{\partial \tau^2} \right\rangle_{\theta, f} , \tag{3.1c}$$

$$Q_{01}(\tau, t) = \left\langle R_0(\tau, t) \frac{\partial^2 R_{1F}(\tau, t)}{\partial \tau^2} \right\rangle_{\theta, f} . \tag{3.1d}$$

In terms of these quantities, our expression for the polymer stress tensor σ (2.13) can be concisely written as [inserting only the first term in (2.9) into σ]

$$\sigma = n_p \lim_{t \to \infty} \int_0^{N_0} d\tau [Q_0(\tau, t) + Q_{ff}(\tau, t) + Q_{10}(\tau, t) + Q_{01}(\tau, t)] , \tag{3.2}$$

where the subscript "Langevin" is dropped from now on, with the proper understanding of this different Langevin formalism for the stress tensor. Our next job is to evaluate the Q's of (3.1a)–(3.1d) in the long-time limit.

Using (2.10a), (2.10f'), and (2.6) and averaging over θ and f according to (2.5a) and (2.5b), we find for (3.1a) and (3.1b) after some simple algebra

$$Q_0(\tau, t \to \infty) = Q_0(\tau)$$

$$= - \sum_{p=1}^{\infty} \int_0^{\infty} dt' 2\lambda_p P(t')$$

$$\cdot [P(t')]^T e^{-2\lambda_p t'} \cos^2(\hat{p}\tau) , \tag{3.3}$$

and similarly for $t \to \infty$ dropping the time variable t in all Q's

$$Q_{ff}(\tau) = \int_0^{N_0} d\tau' \int_0^{N_0} d\tau'' \int_0^{\infty} dt' G_0(\tau, \tau' | t') \frac{\partial^2}{\partial \tau^2} G_0(\tau, \tau'' | t') \int_k 2\eta_0 k^2 [P(t') \cdot \mathcal{O}(k)] \cdot [P(t') \cdot \mathcal{O}(k)]^T S_0(k | \tau', \tau'' | \gamma) , \tag{3.4}$$

where the (zero-order) steady-state scattering factor is defined by

$$S_0(k | \tau', \tau'' | \gamma) = \lim_{t \to \infty} \left\langle e^{ik \cdot [R_0(\tau', t) - R_0(\tau'', t)]} \right\rangle_{\theta, f} \tag{3.5}$$

and the Oseen tensor is given by

$$\mathcal{O}(\mathbf{k}) = (1/\eta_0 k^2) T(\mathbf{k}) ,	\qquad (3.6)$$

with $T(\mathbf{k})$ defined in (2.2a); the superscript T denotes transpose operation.

Before proceeding to (3.1c) for Q_{10}, we discuss, in general, preaveraging approximations for hydrodynamic interactions in the present Langevin formalism. Consider a quantity X involving the following average:

$$X = \langle J\{\mathbf{R}_0(\tau,t)\}\{\mathcal{O}(\mathbf{k})e^{i\mathbf{k}\cdot[\mathbf{R}_0(\tau',t')-\mathbf{R}_0(\tau'',t')]}\}_{\tau'\tau''}\rangle_{\theta,\mathrm{f}} ,$$

where J is an arbitrary function and the $\{\ \}_{\tau'\tau''}$ involves the hydrodynamic interaction between polymer segments τ' and τ'' in Fourier space. The preaveraging approximation means breaking X into two separate averages as

$$X^{(\mathrm{pre})} = \langle J\{\mathbf{R}_0(\tau,t)\}\rangle_{\theta,\mathrm{f}}\langle \mathcal{O}(\mathbf{k})e^{i\mathbf{k}\cdot[\mathbf{R}_0(\tau',t')-\mathbf{R}_0(\tau'',t')]}\rangle_{\theta,\mathrm{f}} ,$$

so that the hydrodynamic interaction is now replaced by its mean value. Clearly such an approximation is unnecessary in the present theory since we know how to perform the average $\langle\ \rangle_{\theta,\mathrm{f}}$ according to (2.5a) and (2.5b). Nevertheless, the preaveraging approximation as described above can often immensely simplify algebraic computations. It is noted that this approximation is *equivalent* to the self-consistent preaveraging approximation (SCPA) introduced by Ottinger in his treatment of hydrodynamic interactions.[10] Consequently, with the preaveraging approximation described above, we anticipate similar results[10] as obtained previously using the numerically implemented SCPA.

It is straightforward to show $Q_{01} = (Q_{10})^T$, so that only the evaluation of Q_{10} is needed. Further calculations lead to the following exact expression for Q_{10}:

$$Q_{10} = Q_{10}^{(\mathrm{pre})} + Q_{10}^{(\mathrm{npc})} ,	\qquad (3.7)$$

where the superscript (pre) designates use of the preaveraging approximation and (npc) corresponds to contributions from fluctuations of hydrodynamic interactions (HI), i.e., nonpreaveraging corrections to the preaveraged value. The preaveraging result is given by

$$Q_{10}^{(\mathrm{pre})}(\tau) = \int_0^{N_0} d\tau' \int_0^{N_0} d\tau'' \int_0^{\infty} dt' \int_0^{\infty} dt'' G_0(\tau,\tau'|t') G_1(\tau,\tau''|t'+2t'')$$

$$\times \int_{\mathbf{k}} P(t')\cdot\mathcal{O}(\mathbf{k})\cdot P(t'')\cdot[P(t'+t'')]^T S_0(\mathbf{k}|\tau',\tau''|\gamma) ,	\qquad (3.7a)$$

where G_1 is defined by

$$G_1(\tau,\tau''|t) = (2/N_0) \sum_{p=1}^{\infty} 2\lambda_p \hat{p}^2 \cos(\hat{p}\tau)\cos(\hat{p}\tau'')e^{-\lambda_p t} .$$

Fluctuations in HI gives rise to a more lengthy expression

$$Q_{10}^{(\mathrm{npc})}(\tau) = -\int_0^{N_0} d\tau' \int_0^{N_0} d\tau'' \int_0^{\infty} dt' \int_0^{\infty} dt_1 \int_0^{\infty} dt_2 G_0(\tau,\tau'|t') G_2(\tau,\tau',\tau''|2t_1,t'+2t_2)$$

$$\times \int_{\mathbf{k}} P(t')\cdot O(\mathbf{k})\cdot\{P(t_1)\cdot[\mathbf{k}\cdot P(t_1)]\}$$

$$\times \{P(t'+t_2)\cdot[\mathbf{k}\cdot P(t_2)]\} S_0(\mathbf{k}|\tau',\tau''|\gamma) ,	\qquad (3.7b)$$

where G_2 is a double summation over polymer modes,

$$G_2(\tau,\tau',\tau''|2t_1,t'+2t_2) = (2/N_0)^2 \sum_{p_1=1}^{\infty} \sum_{p_2=1}^{\infty} 4\lambda_{p_1}\lambda_{p_2}\cos(\hat{p}_2\tau)\cos(\hat{p}_1\tau'')[\cos(\hat{p}_1\tau')-\cos(\hat{p}_1\tau'')]$$

$$\times [\cos(\hat{p}_2\tau')-\cos(\hat{p}_2\tau'')]e^{-2\lambda_{p_1}t_1-\lambda_{p_2}(t'+2t_2)} .$$

In principle there is no guarantee that the mean-field preaveraging value (3.7a) is much larger than its correction (3.7b) due to HI fluctuations. In fact such preaveraging approximations for HI are shown below to be crude, leading to the possibly incorrect results.

B. Preaveraging results

According to (3.2) and (3.7), we define the preaveraged part of σ as

$$\sigma^{(\mathrm{pre})} = n_p \int_0^{N_0} d\tau\{Q_0(\tau)+Q_{ff}(\tau)+Q_{10}^{(\mathrm{pre})}(\tau)$$

$$+[Q_{10}^{(\mathrm{pre})}(\tau)]^T\} .	\qquad (3.8)$$

In order to proceed with the evaluation of (3.8), we need to know γ in (2.10b) which appears in (3.3), (3.4) and (3.7a), (3.7b). In this paper we consider a *simple shear* flow which is a most widely studied flow for polymers. Thus the velocity gradient tensor γ introduced in (2.1) is specified as

$$\gamma_{12} = \dot{\gamma}, \quad \gamma_{ij} = 0 \quad \text{otherwise} ,	\qquad (3.9)$$

where subscript 1 denotes the x direction of shear flow and 2 that of the velocity gradient perpendicular to 1, e.g., the y direction. The scattering factor S_0 in a shear flow is first calculated by inserting (2.10a) with (2.10b)–(2.10d) and (3.9) into (3.5),

$$S_0(\mathbf{k}|\tau',\tau''|\dot\gamma)=e^{-k^2|\tau'-\tau''|/2-ak_1k_2-bk_1^2} ,\qquad (3.10a)$$

where the subscripts i on k indicates the ith Cartesian component of $\mathbf{k}$ and the quantities a and b have the following forms, respectively:

$$a =(2/N_0)\sum_{p=1}^{\infty} (2\hat p^{\,2})^{-1}(\dot\gamma/\lambda_p)$$

$$\times[\cos(\hat p\tau')-\cos(\hat p\tau'')]^2 ,\qquad (3.10b)$$

$$b =\tfrac{1}{2}(2/N_0)\sum_{p=1}^{\infty} (2\hat p^{\,2})^{-1}(\dot\gamma/\lambda_p)^2$$

$$\times[\cos(\hat p\tau')-\cos(\hat p\tau'')]^2 .\qquad (3.10c)$$

Due to shear flow, the scattering factor is no longer isotropic in $\mathbf{k}$ space as a result of chain deformation. This flow-induced chain deformation also affects hydrodynamic interactions (HI) among chain segments since HI explicitly depends on chain configurations. Consequently, the Oseen tensor $\mathcal{O}(\mathbf{k})$ for HI is modified by the presence of the matrices P as shown in (3.7a)–(3.7b).

Substituting (3.4) and (3.7a) into (3.8), we obtain

$$\sigma^{(\mathrm{pre})}(\dot\gamma)=-n_p\sum_{p=1}^{\infty}\begin{vmatrix} 2(\dot\gamma_p^{\,0})^2 & \dot\gamma_p^{\,0} & 0 \\ \dot\gamma_p^{\,0} & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix}$$

$$+n_p\sum_{p=1}^{\infty}\int_0^{N_0}d\tau'\int_0^{N_0}d\tau''(2/N_0)(\zeta_0/2)\cos(\hat p\tau')\cos(\hat p\tau'')$$

$$\times\int_{\mathbf{k}}\int_0^{\infty}d\alpha\, e^{-\alpha}(1/\eta_0k^2)(L+L^{\,T})S_0(\mathbf{k}|\tau',\tau''|\dot\gamma) ,$$

$$L =P(\alpha\tau_p^0)\cdot T(\mathbf{k})\cdot\begin{vmatrix} (\alpha+2)(\dot\gamma_p^{\,0})^2 & \dot\gamma_p^{\,0} & 0 \\ \dot\gamma_p^{\,0} & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix}$$

$$(3.11)$$

where the dimensionless bare flow parameter is defined by

$$\dot\gamma_0^{\,0}=\dot\gamma\tau_p^0 \qquad (3.12a)$$

with the bare polymer relaxation time given by

$$\tau_p^0 =\tfrac{1}{2}\lambda_p =(\zeta_0/2)(N_0/\pi)^2 p^{-2} .\qquad (3.12b)$$

S_0 has been given by (3.5) and (3.10a)–(3.10c). The isotropic portion of $\sigma^{(\mathrm{pre})}$, involving a unity matrix, is omitted since it only contributes to the hydrostatic pressure.

Since in our continuum chain model no cutoff[19] is introduced along the chain contour to forbid $\tau'=\tau''$ in (3.11), some singularities arises due to short-distance hydrodynamic interactions. This singularity occurs[11] *even* in *absence* of a macroscopic flow (2.1). If we denote the singular part of (3.11) by $\sigma_s^{(\mathrm{pre})}=\sigma^{(\mathrm{pre})}(\dot\gamma=0)$, then the nonsingular part is defined by $\sigma_s^{(\mathrm{pre})}=\sigma^{(\mathrm{pre})}(\gamma)-\sigma^{(\mathrm{pre})}(\dot\gamma=0)$, so that $\sigma^{(\mathrm{pre})}=\sigma_s^{(\mathrm{pre})}+\sigma_{ns}^{(\mathrm{pre})}$. The singular part $\sigma_s^{(\mathrm{pre})}$ involves the isotropic zero flow scattering factor $S_0(\mathbf{k}|\tau',\tau''|\dot\gamma=0)=e^{-k^2|\tau'-\tau''|}$ for which $T(\mathbf{k})$ of (2.2a) can be replaced by the unity matrix $\mathbb{1}$ times $(1-1/d)$ in carrying out the $\mathbf{k}$ integration in (3.11). Then the integration over α can be readily performed, yielding

$$\sigma_s^{(\mathrm{pre})}=-n_p\sum_{p=1}^{\infty}\begin{vmatrix} 2(\dot\gamma_p^{\,0})^2[1-2z_H^0(2/\epsilon-\ln p-f_p)] & \dot\gamma_p^{\,0}[1-z_H^0(2/\epsilon-\ln p-f_p)] & 0 \\ \dot\gamma_p^{\,0}[1-z_H^0(2/\epsilon-\ln p-f_p)] & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} ,\qquad (3.13)$$

where use is made of (A1) for the $\mathbf{k}$ integration and of (B5a) and (B5b) for contour integrations in Appendixes A and B. The function f_p is given in (B5b) and the parameter z_H^0 in (3.13) is the bare hydrodynamic interaction (HI) variable, defined as (here $\epsilon=4-d$, with d being the dimensionality)

$$z_H^0 =(2\pi N_0)^{\epsilon/2}(\zeta_0/\eta_0)[(1-1/d)/(d/2-1)](2\pi)^{-2}=u_H^0(2\pi N_0/L)^{\epsilon/2} ,\qquad (3.14)$$

where the second equality identifies another natural parameter u_H^0 for HI which is independent of chain length N_0, and $2\pi N_0/L$ measures the hydrodynamic "blob" size.[13]

The nonsingular portion of $\sigma^{(\mathrm{pre})}$ is more involved and has the following structure which we derive after integration over α and matrix multiplication in (3.11),

$$\sigma_{ns}^{(pre)}=n_p(2/N_0)(\zeta_0/\eta_0)\sum_{p=1}^{\infty}\dot{\gamma}_p^0\int_0^{N_0}d\tau'\int_0^{N_0}d\tau''\cos(\hat{p}\tau')\cos(\hat{p}\tau'')\int_{\mathbf{k}}k^{-2}[S_0(\mathbf{k}|\tau',\tau''|\dot{\gamma})-S_0(\mathbf{k}|\tau'-\tau''|\dot{\gamma}=0)]M(\mathbf{k},\dot{\gamma}) \ .$$

$$(3.15a)$$

The *symmetric* matrix M is given by

$$M=\begin{vmatrix} -\bar{k}_1\bar{k}_2+(4-3\bar{k}_1^2-\bar{k}_2^2)\dot{\gamma}_p^0-4\bar{k}_1\bar{k}_2(\dot{\gamma}_p^0)^2 & 1-(\tfrac{1}{2})(\bar{k}_1^2+\bar{k}_2^2)-2\bar{k}_1\bar{k}_2\dot{\gamma}_p^0 & -\bar{k}_2\bar{k}_3/2-(\tfrac{3}{2})\bar{k}_1\bar{k}_3\dot{\gamma}_p^0 \\ 1-(\tfrac{1}{2})(\bar{k}_1^2+\bar{k}_2^2)-2\bar{k}_1\bar{k}_2\dot{\gamma}_p^0 & -\bar{k}_1\bar{k}_2 & -(\tfrac{1}{2})\bar{k}_1\bar{k}_3 \\ -\bar{k}_2\bar{k}_3/2-(\tfrac{3}{2})\bar{k}_1\bar{k}_3\dot{\gamma}_p^0 & -(\tfrac{1}{2})\bar{k}_1\bar{k}_3 & 0 \end{vmatrix}, \quad (3.15b)$$

where $\bar{\mathbf{k}}=\mathbf{k}/k$ with the subscript i on $\bar{k}$ denoting the ith Cartesian direction, as specified in (3.9), and $\dot{\gamma}_p^0$ has been defined before in (3.12a).

The presence of $1/\epsilon$ pole terms in (3.13) is due to use of the continuum chain model and to the neglect of a cutoff in hydrodynamic interactions[19] and therefore requires a Gell-Mann–Low–type "mass" renormalization. These singular terms (singular as $\epsilon\to0$) can be removed through the following renormalization procedure. The renormalized variable u_H is related to the bare u_H^0 through the expression $u_H^0=u_H[1+(2/\epsilon)u_H+\cdots]$; then according to (3.12b) and (3.14), the bare relaxation times τ_p^0 also need to be renormalized as $\tau_p^0=\tau_p[1+(2/\epsilon)u_H+\cdots]$. The renormalized $\sigma_s^{(pre)}$ has the form

$$\sigma_s^{(pre)}=-n_p\sum_{p=1}^{\infty}\begin{vmatrix} 2(\dot{\gamma}\bar{\tau}_p)^2(1+2u_Hf_p) & \dot{\gamma}\bar{\tau}_p(1+u_Hf_p) & 0 \\ \dot{\gamma}\bar{\tau}_p(1+u_Hf_p) & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix},$$

$$(3.16)$$

where the Rouse-Zimm relaxation times are defined as

$$\bar{\tau}_p=\tau_p(2\pi N_0/L)^{-u_H} \ , \qquad (3.17a)$$

with the parameter τ_p defined by

$$\tau_p=(\zeta/2)(N_0/\pi)^2p^{-2+u_H} \ . \qquad (3.17b)$$

The renormalized friction ζ is related to u_H in the same way as ζ_0 is related to u_H^0 in (3.14). Thus $\bar{\tau}_p$ scales with the chain length N_0 as $N_0^{2-u_H}$, namely, $\bar{\tau}_p\sim N_0^{3/2}$ in the strong hydrodynamic interaction (HI)—Zimm chain—limit (i.e., at the nondraining fixed point $u_H^*=\epsilon/2=\tfrac{1}{2}$, $d=3$). When excluded volume interactions are present the scaling law is modified as $\tau_p\sim N_0^{3\nu}$ for the Zimm chain with $\nu\approx0.6$.

In this paper we are interested in the evaluation of the second normal stress difference for reasons that will be clear later. To this end, we consider the second and third diagonal elements of $\sigma^{(pre)}$ in (3.8). Since these two elements are zero in $\sigma_s^{(pre)}$ of (3.16) we are only concerned with those of $\sigma_{ns}^{(pre)}$ in (3.15a) and (3.15b). In particular, we write down their difference

$$\sigma_{22}^{(pre)}-\sigma_{33}^{(pre)}=(\sigma_{ns}^{(pre)})_{22}$$

$$=-n_pu_H[d(d-2)/(d-1)](2\pi)^2(\dot{\gamma}\bar{\tau}_1)\int_0^1dx'\int_0^1dx''\sum_{p=1}^{\infty}p^{-2}\cos(\pi px')\cos(\pi px'')K_{12}(x',x'') \ , \qquad (3.18)$$

where K_{12} is given by

$$K_{12}(x',x'')=\int_{\mathbf{q}}q_1q_2q^{-4}[S_0(\mathbf{q}|x',x''|\dot{\gamma})$$

$$-S_0(\mathbf{q}|x',x''|\dot{\gamma}=0)] \ , \quad (3.19a)$$

with S_0's given by (3.10a)–(3.10c), where $x'=\tau'/N_0$ and $q=kN_0^{-1/2}$. The explicit result for K_{12} is presented in Appendix A and here we expand it to first order in the dimensionless flow parameter $\dot{\gamma}\bar{\tau}_1$ to obtain

$$K_{12}=-(\tfrac{1}{576})(\dot{\gamma}\bar{\tau}_1)[3(x'+x'')-|x'-x''|$$

$$-(\tfrac{3}{2})(x'+x'')^2]+O[(\dot{\gamma}\bar{\tau}_1)^3] \ . \quad (3.19b)$$

Using the identity (B1) in Appendix B, and inserting (3.19b) into (3.18), we finally arrive at the *preaveraged* second normal stress difference to $O(\epsilon)$, with aid of (B6) for the double integration over x' and x'',

$$\sigma_{22}^{(pre)}-\sigma_{33}^{(pre)}=\sigma_{22}^{(pre)}$$

$$=-n_pu_H(\pi^4/38\,880)(\dot{\gamma}\bar{\tau}_1)^2+O[(\dot{\gamma}\bar{\tau}_1)^4] \ , \qquad (3.20)$$

where n_p is the polymer number density, u_H is the hydrodynamic interaction parameter, $\dot{\gamma}$ is the shear rate, and $\bar{\tau}_1$

is the longest polymer relaxation time. We note that within the preaveraging approximation $\sigma_{33}^{(\text{pre})}=0$, as is evident from (3.15b). Thus a *negative* $\sigma_{22}^{(\text{pre})}$ shown in (3.20) tells us that in a two-parallel-plate device which generates the simple shear flow, the force due to polymers on any surface in the solution parallel to the middle $y=0$ plane would be directed towards the latter. This is just the opposite to our anticipation that *elastic* polymer chains should resist their deformation—they are compressed by flow in the y direction—and produce outward forces on the two plates.[3] Similar unphysical results have been found in previous consistent preaveraging calculations[10] using the Kirkwood diffusion equation theory. All this suggests that the preaveraging approximation could be seriously in error and should be avoided when describing the compression in the direction of velocity gradient.

C. Nonpreaveraging correction

The preaveraging approximation for hydrodynamic interactions would be a *good* one *if* the solvent motion was so slow that the polymer chain had enough time to sample all of its conformations before hydrodynamic disturbances could propagate appreciable distance between chain segments. In reality, it is the opposite which is true: namely, the solvent dynamics is always much faster than that of a long polymer.[18] Therefore it is crucial that we be able to correctly describe hydrodynamic interactions in a chain. This implies that we must incorporate the nonpreaveraging corrections neglected in Sec. III B. Inserting (2.10c) into (3.7b) and integrating over τ according to (3.2) and (3.7), the "fluctuating" part of the stress tensor for a general homogeneous flow (2.1) is found to have the form

$$\sigma^{(\text{npc})}=\int_0^{N_0}d\tau[Q_{10}^{(\text{npc})}+(Q_{10}^{(\text{npc})})^T]$$

$$=-(n_p/2)(2/N_0)^2\sum_{p_1=1}^{\infty}\sum_{p_2=1}^{\infty}\int_0^{N_0}d\tau'\int_0^{N_0}d\tau''\cos(\hat{p}_1\tau')\cos(\hat{p}_2\tau'')[\cos(\hat{p}_1\tau')-\cos(\hat{p}_1\tau'')][cos(\hat{p}_2\tau')-\cos(\hat{p}_2\tau'')]$$

$$\times\int_0^{\infty}dt'\int_0^{\infty}dt_1\int_0^{\infty}dt_2 e^{-t'-t_1-t_2}\int_{\mathbf{k}}S_0(\mathbf{k}|\tau',\tau''|\dot{\gamma})(\mathcal{T}+\mathcal{T}^T)\ ,$$

$$\mathcal{T}=[\bar{\tau}_{p_2}\mathbf{A_k}(21)\mathbf{B_k}(2)+(1\leftrightarrow2)]\quad(3.21)$$

where vector functions $\mathbf{A_k}$ and $\mathbf{B_k}$ are, respectively, defined as

$$\mathbf{A_k}(21)=P(t',p_2)\cdot\mathcal{O}(\mathbf{k})\cdot a_1,\quad \mathbf{B_k}(2)=P(t',p_2)\cdot a_2\ ,\quad(3.21a)$$

with $a_i=P(t_i,p_i)\cdot[\mathbf{k}\cdot P(t_i,p_i)]$ and $P(t,p_i)=e^{\dot{\gamma}_{p_i}t}$. The renormalized dimensionless flow parameter $\dot{\gamma}_p$ is related to the shear rate as $\dot{\gamma}\bar{\tau}_p=\dot{\gamma}_p$. $\mathcal{T}$ in (3.21) is a $d\times d$ matrix and its transpose is given by the last term in the last set of parentheses. The difference between the second and third diagonal elements of $(\mathcal{T}+\mathcal{T}^T)$ has the truncated form (to the lowest nontrivial order in $\dot{\gamma}_p$) after integrations over t', t_1, and t_2

$$\dot{\gamma}\bar{\tau}_{p_1}\bar{\tau}_{p_2}[2k_1k_2(1-2\bar{k}_2^2+2\bar{k}_1^2)+k_1^2(1-4\bar{k}_2^2+2\bar{k}_3^2)(\dot{\gamma}_{p_1}+\dot{\gamma}_{p_2})]\ ,\quad(3.21b)$$

where $\bar{k}_i$'s are defined below (3.15b). Thus the nonpreaveraging portion of the second normal stress is given by, with the aid of (A4)–(A8) in the Appendix A

$$\sigma_{22}^{(\text{npc})}-\sigma_{33}^{(\text{npc})}=-(8n_p/3)u_H(\dot{\gamma}\bar{\tau}_1)^2$$

$$\times\sum_{p_1=1}^{\infty}\sum_{p_2=1}^{\infty}\int_0^1dx'\int_0^1dx''p_1^{-2}p_2^{-2}(x'-x'')^{-2}\cos(\pi p_1 x')\cos(\pi p_2 x'')$$

$$\times[\cos(\pi p_1 x')-\cos(\pi p_1 x'')][\cos(\pi p_2 x')-\cos(\pi p_2 x'')]$$

$$\times\{-(\tfrac{1}{36})|x'-x''|[3(x'+x'')-|x'-x''|-(\tfrac{3}{2})(x'+x'')^2]+(1/6\pi^2)(p_1^{-2}+p_2^{-2})\}.$$

$$(3.22)$$

Substituting (B4) for the double summation over p_1 and p_2 into (3.22) and using (B2) and (B3), we find the value for (3.22), according to (B7) and (B8) for the twofold integrals over x' and x'',

$$\sigma_{22}^{(\text{npc})}-\sigma_{33}^{(\text{npc})}=n_p u_H(41\pi^4/68\,040)(\dot{\gamma}\bar{\tau}_1)^2+O((\dot{\gamma}\bar{\tau}_1)^4)\ .$$

$$(3.23)$$

Notice that this nonpreaveraging correction to the second normal stress tensor is much larger in magnitude than its preaveraged value (3.20) and has an *opposite* sign.

It is convenient to define the second normal stress coefficient Ψ_2 through $\sigma_{22}-\sigma_{33}=-\Psi_2\dot{\gamma}^2$ so that according to (3.20) and (3.23) we have, respectively, the *preaveraged* Ψ_2,

$$\Psi_2^{(\text{pre})} = 2.23 \times 10^{-4} cM ([\eta]_0 \eta_0)^2 / RT , \qquad (3.24)$$

and the *unpreaveraged* Ψ_2,

$$\Psi_2 = -5.00 \times 10^{-2} cM ([\eta]_0 \eta_0)^2 / RT , \qquad (3.25)$$

where Ψ_2 has been given in terms of experimental observables: c is the polymer concentration, M is the polymer's molecular weight, $[\eta]_0$ is the intrinsic viscosity at zero shear rate, R the gas constant, and T the temperature. In the transition from (3.20) and (3.23) to (3.24) and (3.25), we have used the relationship[5] between the longest relaxation time $\bar{\tau}_1$ and the zero shear intrinsic viscosity: $\bar{\tau}_1 \approx 0.422 [\eta]_0 \eta_0 / RT$. Here Ψ_2's are obtained for small shear rates so that Ψ_2 is independent of $\dot{\gamma}$, the shear rate.[20] In general, material functions of polymer solutions such as Ψ_2 and the intrinsic viscosity are functions of the dimensionless flow parameter $\dot{\gamma} \bar{\tau}_1$.

IV. DISCUSSION

With the second normal stress Ψ_2 as an example, we have considered the analytical evaluation of the stress tensor using coupled Langevin equations for polymer-solvent dynamics. The distinct advantage of pursuing such an alternative path to polymer dynamics and rheology lies in the fact that in *presence* of a macroscopic *flow* it offers a *more direct* formulation of the dynamic motion of polymer chains and a *more convenient* treatment of hydrodynamic interactions between polymer segments. This superiority arises from the significant difference between the present Langevin formalism and the more familiar Kirkwood diffusion equation approach. In our formulation the effect of flow on a polymer chain is described by a Langevin dynamic equation so that the solution for its dynamic motion $\{ \mathbf{R}_i(t) \}$ contains *all* the nonequilibrium information involving flow. By contrast, in the Kirkwood diffusion equation formalism the effects of flow are reflected *solely* in the nonequilibrium distribution function P for polymer configurations, a steady-state solution to the Kirkwood diffusion equation. This difference should be evident from some of previous studies,[13] but unfortunately it was not as fully recognized before.

Very often mean-field-type preaveraging approximations or some other approximations are necessarily invoked in dealing with the Kirkwood diffusion equation or with equations of its moments,[10] leading to undesirable results. Here no such approximations are needed anywhere so that we are able to assess the validity of these approximations. Clearly the preaveraging approximation of hydrodynamic interactions (HI) is rather severe because propagation of the solvent mediated HI at length scales of a polymer chain is very fast in terms of polymer relaxation times. For example, the typical time scale for propagation of HI through a distance of the polymer size R_G is $\rho_0 (R_G)^2 / \eta_0$ while the overall polymer relaxation time is $\eta_0 (R_G)^3 / k_B T$, much larger than the former for a long polymer chain in a typical solvent. Consequently the propagation of HI—depending on the *instantaneous* configuration of a polymer chain—can *not* be faithfully described by its average over all the chain configurations, as implied in the preaveraging approximation.

By *numerically* analyzing the Kirkwood diffusion equation[21] with consistent preaveraging approximation, previous studies obtain a positive value for Ψ_2, whereas it should be negative. It was thus natural for us to demonstrate that avoidance of preaveraging approximations leads[21] to a *negative* Ψ_2. In this paper, the serious errors due to the preaveraging approximation (PA) are examined by calculating the second normal stress Ψ_2, both with and without using this approximation (in Sec. III B and III C, respectively). Indeed, with the PA, we find positive Ψ_2 in coincidence with previous theoretical studies.[10] Indeed, *without* using the PA we *analytically* obtain for the first time a negative Ψ_2 in (3.25) for a continuum polymer chain which is much larger in magnitude than the preaveraged value in (3.24). This is the reason for first calculating the basic material function Ψ_2 in this paper, studies of many other polymer properties will be pursued in later work following the Langevin formulation presented here.

We have confined ourselves to considering the small shear rate limit in the evaluation of the second normal stress. In this limit we have obtained analytical results. However, the power of the present Langevin theory lies precisely in its ability to deal with *strong* homogeneous and inhomogeneous flows while avoiding implementation of mean-field preaveraging approximations. Future studies employing this formalism will explicitly treat *strong* shear flows and evaluate, among other properties, intrinsic shear viscosity and the radius of gyration of a single chain in flow, as a function of the shear rate.

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APPENDIX A

Derivation of (3.13) involves the following integration:

$$\int_{\mathbf{k}} k^{-2} e^{-k^2 |\tau' - \tau''|/2} = [1/(d-2)](2\pi)^{-d/2} |\tau' - \tau''|^{\epsilon/2 - 1} ,$$

$$\epsilon = 4 - d . \qquad (A1)$$

The integral in (3.19a) can be evaluated by introducing the identity

$$\int_0^\infty d\alpha \, \alpha e^{-q^2 \alpha} = q^4$$

into the former, permitting the $\mathbf{q}$ integration. Then, it is found

$$K_{12} = 2^{-d} \pi^{-d/2} A \dot{\gamma}_1 |x' - x''|^{-1}$$
$$\times \int_0^1 dx (1-x) x [1 + (Bx - A^2 x^2) \dot{\gamma}_1^2]^{-3/2}$$
$$= 2^{-d} \pi^{-d/2} A \dot{\gamma}_1 |x' - x''|^{-1} [\tfrac{1}{6} + O(\dot{\gamma}_1^2)] , \qquad (A2)$$

where A and B are functions of x' and x'' and are

defined, respectively, as

$$A = (2/\pi^2)|x'-x''|^{-1}\sum_{p=1}^{\infty}p^{-4}[\cos(\pi px')-\cos(\pi px'')]^2$$

$$= (\pi^2/6)|x'-x''|[3(x'+x'')-|x'-x''|$$

$$-(\tfrac{3}{2})(x'+x'')^2]\ , \tag{A3a}$$

and

$$B = (4/\pi^2)|x'-x''|^{-1}\sum_{p=1}^{\infty}p^{-6}[\cos(\pi px')-\cos(\pi px'')]^2\ , \tag{A3b}$$

and the flow parameter is given by $\dot{\gamma}_1 = \dot{\gamma}\bar{\tau}_1$. The second equality in (A2) gives (3.19b) for $d=4$, although (A1) can be analytically integrated without the expansion in powers of $\dot{\gamma}_1$.

Similarly, integrals corresponding to (3.21b) are given as follows. To the lowest nontrivial order in $\dot{\gamma}_1$, we have

$$K(12) = \int_{\mathbf{q}} q_1 q_2 q^{-2} S_0(\mathbf{q}|x',x''|\dot{\gamma})$$

$$= -(\tfrac{1}{6})(2\pi)^{-2} A\dot{\gamma}_1 |x'-x''|^{-2} + O(\dot{\gamma}_1^3)\ , \tag{A4}$$

$$K(12^3) = \int_{\mathbf{q}} q_1 q_2^3 q^{-4} S_0(\mathbf{q}|x'-x''|\dot{\gamma})$$

$$= -(\tfrac{1}{16})(2\pi)^{-2} A\dot{\gamma}_1 |x'-x''|^{-2} + O(\dot{\gamma}_1^3)\ , \tag{A5}$$

$$K(123^2) = \int_{\mathbf{q}} q_1 q_2 q_3^2 q^{-4} S_0(\mathbf{q}|x',x''|\dot{\gamma})$$

$$= -(\tfrac{1}{48})(2\pi)^{-2} A\dot{\gamma}_1 |x'-x''|^{-2} + O(\dot{\gamma}_1^3)\ , \tag{A6}$$

$$K(1^2 2^2) = \int_{\mathbf{q}} q_1^2 q_2^2 q^{-4} S_0(\mathbf{q}|x'-x'')|\dot{\gamma})$$

$$= (\tfrac{1}{24})(2\pi)^{-2}|x'-x''|^{-2} + O(\dot{\gamma}_1^2)\ , \tag{A7}$$

$$K(1^2) = \int_{\mathbf{q}} q_1^2 q^{-2} S_0(\mathbf{q}|x',x''|\dot{\gamma})$$

$$= (\tfrac{1}{4})(2\pi)^{-2}|x'-x''|^{-2} + O(\dot{\gamma}_1^2)\ , \tag{A8}$$

where A is given in (A3a).

APPENDIX B

Calculations in this paper often involve summations over polymer normal modes. Here are some of the relevant sums required in our evaluation of the stress tensor:

$$\sum_{p=1}^{\infty}p^{-2}\cos(\pi px')\cos(\pi px'') = (\pi^2/2)[\tfrac{1}{3} - (\tfrac{1}{2})(x'+x''+|x'-x''|) + (\tfrac{1}{2})(x'^2+x''^2)]\ , \tag{B1}$$

$$\sum_{p=1}^{\infty}p^{-2}\cos(\pi px')[\cos(\pi px')-\cos(\pi px'')] = (\pi^2/4)[x''-x'+|x'-x''|+(x'^2-x''^2)]\ , \tag{B2}$$

$$\sum_{p=1}^{\infty}p^{-2}\cos(\pi px'')[\cos(\pi px')-\cos(\pi px'')] = (\pi^2/4)[x''-x'-|x'-x''|+(x'^2-x''^2)]\ , \tag{B3}$$

$$I(x',x'') = \sum_{p_1=1}^{\infty}\sum_{p_2=1}^{\infty}p_1^{-2}p_2^{-2}(p_1^{-2}+p_2^{-2})(x'-x'')^{-2}\cos(\pi p_1 x')\cos(\pi p_2 x'')$$

$$\times[\cos(\pi p_1 x')-\cos(\pi p_1 x'')][\cos(\pi p_2 x')-\cos(\pi p_2 x'')]$$

$$= (\pi^6/48)\{[2-(x'+x'')](x'+x'')[1-3x'+(\tfrac{1}{4})(x''^2+7x'^2)]$$

$$-(x'+x'')[x'+x''-(x'^2+4x''^2+x'x'')+(\tfrac{1}{4})(x'^3+7x''^3+7x''^2 x'+x''x'^2)]\}\ , \tag{B4}$$

which has been obtained for $x'>x''$.

To get (3.13) we need to perform the following twofold integral:

$$\int_0^1 dx'\int_0^1 dx''\cos(\pi px')\cos(\pi px'')|x'-x''|^{\epsilon/2-1} = 2/\epsilon - \ln p - f_p + O(\epsilon)\ , \tag{B5a}$$

where the mode-dependent function f_p is given by

$$f_p = C + \ln\pi - \text{ci}(\pi p) + (1/\pi p)[\text{si}(\pi p) + \pi/2]\ . \tag{B5b}$$

C is the Euler's constant (≈ 0.577), ci(x) and si(x) are cosine and sine integral functions. Also involved in our calculations are some other two-dimensional integrals whose values are listed as follows:

$$\int_0^1 dx'\int_0^1 dx''[\tfrac{1}{3}-(\tfrac{1}{2})(x'+x''+|x'-x''|)+(\tfrac{1}{2})(x'^2+x''^2)][3(x'+x'')-|x'-x''|-(\tfrac{3}{2})(x'+x'')^2] = -\tfrac{1}{360}\ , \tag{B6}$$

$$\int_0^1 dx'\int_0^{x'} dx''[2-(x'+x'')](x'^2-x''^2)[2x'+4x''-(\tfrac{3}{2})(x'+x'')^2] = \tfrac{163}{1260}\ , \tag{B7}$$

$$\int_0^1 dx'\int_0^{x'} dx'' I(x',x'')(48/\pi^6) = -\tfrac{7}{72}\ , \tag{B8}$$

where $I(x',x'')$ is defined in (B4).

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[18]Here we are concerned with solvent dynamics and its velocity fields at length scales comparable to the polymer size. At such scales, the propagation of dynamic disturbances is very fast in terms of the time scale of polymer Brownian movement. Thus hydrodynamic interactions can be regarded as instantaneous so that the static Oseen tensor description is valid, as given in (2.6).

[19]Occurrence of such singular terms are common in the continuum modeling of the polymer chain and renormalization procedures are standard, e.g., see Ref. 13 and S. Q. Wang, J. F. Douglas, and K. F. Freed, J. Chem. Phys. **85**, 3674 (1986); **87**, 1346 (1987).

[20]In this small shear rate limit, the first normal stress coefficient Ψ_1, defined similarly as $\sigma_{11} - \sigma_{22} = -\Psi_1 \dot{\gamma}^2$, can be derived from Ref. 5 as $\Psi_1 = 0.41 cM ([\eta]_0 \eta)^2 /RT$. Thus we obtain a ratio $\Psi_2/\Psi_1 \approx -1\%$, as expected (see Ref. 3).

[21]Using self-consistent preaveraging approximations, Ottinger first finds a positive second normal stress in J. Chem. Phys. **86**, 3731 (1987). Subsequently he introduces the Gaussian approximation to avoid preaveraging of the hydrodynamic Oseen tensor in J. Chem. Phys. **90**, 565 (1989) and obtains a negative Ψ_2 for a *dumbbell* model of polymers. While this manuscript was being prepared, unpublished work by H. C. Ottinger and Y. Rabin was brought to our attention, where they also arrived at the nonpreaveraging correction (3.23). Thus, both the Kirkwood diffusion equation and the Langevin approach give the same results for material functions in the limit of small shear rates. However, since the equivalence between the present Langevin method and the Kirkwood diffusion equation approach has not been *rigorously* established for strong flows, relation between the two methods is not entirely clear.