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# Langevin dynamics of Rouse chains under flow

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A systematic approach is developed for describing the hydrodynamics of flowing polymer solutions by using a microscopic Langevin model for which the inertial nonlinearities and solvent advection are ignored. The influence of polymer motion on the solution velocity field is evaluated by averaging over the polymer degrees of freedom at a time in the distant past in order to derive an effective hydrodynamic equation of motion for the averaged polymer solution. The polymer's contribution to the fluid stress tensor is computed from the total solution stress tensor whose divergence appears in the averaged effective hydrodynamic equation. Introduction of the Rouse chain and long wavelength limits enables the analytical evaluation of this stress tensor for any time-dependent linear flows. All the material functions for the polymer solution are evaluated in a simplified fashion for these flows, recovering some known results and deriving several new ones.

## I. INTRODUCTION

The dynamics of polymers in solution has been of interest from two rather differing perspectives. On the one hand, transport properties of dilute polymer solutions are widely used as a means for characterizing the polymers on a molecular scale, while rheologists, on the other hand, focus on the complicated non-Newtonian flow characteristics of the polymer solutions.<sup>1</sup> A molecular understanding within both of these perspectives is beset by fundamental theoretical difficulties arising from the complexity of the many-body problems inherent in the mathematical description of the coupled polymer-solvent dynamics.

While a great deal of progress has been made in understanding the chain-like molecular basis for polymer transport processes in dilute polymer solutions,<sup>2,3</sup> rather little has been accomplished in the development of molecular based theories of the flow properties of these solutions. In fact, most of the work on this subject has been purely phenomenological, using the methods of continuum mechanics and postulated constitutive equations<sup>4</sup> that relate the solution stress tensor to the strain rate in the fluid. Much of the available molecular based treatments of the flow involve<sup>4</sup> the use of oversimplified models to eliminate the mathematical complexities associated with the presence of many internal degrees of freedom in flexible polymers.

Some of the recent advances in the theory of polymer-flow interactions have benefited from the work of Onuki and Kawasaki<sup>5</sup> on the critical dynamics of fluids under shear flow where they use coupled kinetic equations and renormalization group methods. The majority of the polymer work considers the polymer transport properties and not the fluid flow, but the latter advances now provide sufficient theoretical input to permit a consideration of the flow problems. The work on polymer transport properties includes that of Oono and co-workers who have been applying the Langevin kinetic equations method to the calculation of the diffusion coefficient,

the intrinsic viscosity and the dynamical chain correlation functions for a polymer chain in the limit of zero shear rate<sup>6</sup> and of the dynamical mean square end vector for a Gaussian chain in systematic flows.<sup>7</sup> Schaub and co-workers<sup>8</sup> have also used these methods to perform computations of the polymer transport properties of dilute polymer solutions without flow.

Several studies<sup>9-11</sup> of polymer solutions subjected to strong flows have emphasized the alteration of the conformation and dynamics of the polymers in strong flows, but these works do not address the question of the description of the effective non-Newtonian behavior of the solution hydrodynamics. Only rather recently has Rabin<sup>12</sup> considered the modification of the fluid flow arising in polymer solutions undergoing the coil-stretch transition, and Friedman and Rabin have recently also studied<sup>13,14</sup> the effective hydrodynamics of dilute solutions of Rouse model polymers in the limit of zero flow.

Here we study the hydrodynamics of polymers under systematic flows which are below the critical strain rate necessary to induce the coil-stretch transition. Thus, it is permissible to utilize simple, Gaussian chain models of the polymer and to avoid the enormous mathematical complexities associated with the need of non-Gaussian models for describing the coil-stretch transition. Fluid convection is ignored, and this also limits the maximum applicable shear rate for which the model is valid. We use the coupled kinetic Langevin equations formulation but consider the low frequency limit where the dynamics of the Oseen tensor may be neglected and steady-state hydrodynamics may be applied to the solvent dynamics. Given this well defined and well studied limit, we consider the general hydrodynamics of a solution of Gaussian polymers. The general theory is specialized to the dilute solution Rouse<sup>2,3</sup> chain limit where explicit computations are provided for the constitutive equations describing the strain rate dependence of the polymers' contribution to the averaged solution stress tensor. Our formal development also fully includes the hydrodynamic interactions which, in principle, could be treated explicitly within a

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renormalization group formulation. The Rouse limit considered here, therefore, corresponds to the zeroth order term in such a treatment which we plan to pursue in the future.

Section II describes the kinetic model, while the general scheme for formal solution of these equations is given in Sec. III. The dilute solution, Rouse limit of the formal solutions is taken in Sec. IV where the effective Navier–Stokes equation for the conformally averaged polymer solution is derived. This Rouse model is solved exactly in Sec. V in the long wavelength limit where constitutive equations are derived for elongational flows and simple shear. Because of our use of a Gaussian chain model, the constitutive equations for elongational flows exhibit unphysical behavior as the coil–stretch transition is approached, but the equations are well defined for arbitrary shear rates in simple shear flow, provided the shear rate is low enough that nonlinearities produced by fluid convection may be neglected. Some of our steady state results reproduce previously derived<sup>2,4</sup> information for simple shear flow, but new material functions are also obtained in Sec. VI for elongational flows, for oscillatory shear and elongational flows, and for stress relaxation.

## II. MODEL

The kinetic model for polymer dynamics<sup>6</sup> is described by a pair of coupled Langevin equations. For simplicity, we consider the case of a continuous Gaussian chain in a continuum solvent in which the polymer equation is given by the force balance

$$\frac{\partial}{\partial t} \mathbf{c}(\tau, t) - \mathbf{u}[\mathbf{c}(\tau, t), t] = \xi_0^{-1} \frac{\partial^2}{\partial \tau^2} \mathbf{c}(\tau, t) + \boldsymbol{\theta}(\tau, t), \quad (2.1)$$

where  $\mathbf{c}(\tau, t)$  designates the position of the polymer segment at the contour point  $\tau$  along the continuous chain of length  $N_0$  at time  $t$ . [ $\mathbf{c}(\tau, t)$  is in units of  $(d/l)^{1/2}$  with  $d$  the spatial dimensionality and  $l$  the Kuhn step length.] The quantity  $\mathbf{u}(\mathbf{r}, t)$  is the fluid velocity at the spatial position  $\mathbf{r}$  at time  $t$ ,  $\xi_0$  is the friction coefficient for the chain segment, and the random force  $\boldsymbol{\theta}$  is described in Eq. (2.1a) below.

The dynamical equation for the fluid velocity field is

$$\begin{aligned} & \left( \rho_0 \frac{\partial}{\partial t} - \eta_0 \nabla^2 \right) \mathbf{u}(\mathbf{r}, t) + \rho_0 \mathbf{u} \cdot \nabla \mathbf{u} + \nabla p \\ &= \mathbf{f}(\mathbf{r}, t) + \sum_{\alpha=1}^{n_p} \int_0^{N_0} d\tau_{\alpha} \delta[\mathbf{r} - \mathbf{c}_{\alpha}(\tau_{\alpha}, t)] \frac{\partial^2}{\partial \tau_{\alpha}^2} \\ & \quad \times \mathbf{c}_{\alpha}(\tau_{\alpha}, t), \end{aligned} \quad (2.2)$$

where the condition  $\nabla \mathbf{u} = 0$  implies the incompressibility of the solvent,  $\eta_0$  is the solvent viscosity,  $p$  is the effective hydrostatic pressure in the fluid,  $\rho_0$  is the solvent density, and  $n_p$  is the total number of polymers in the solution. For notational simplicity, Eqs. (2.1) and (2.2) are written with a unit Rouse force constant. Standard units may readily be reintroduced in final equations that are expressed below in terms of Rouse mode relaxation times. The random forces  $\boldsymbol{\theta}$  and  $\mathbf{f}$  each have zero mean and covariances

$$\langle \boldsymbol{\theta}(\tau, t) \boldsymbol{\theta}(\tau', t') \rangle = (2/\xi_0) \delta(\tau - \tau') \delta(t - t') \mathbf{1}, \quad (2.1a)$$

$$\langle \mathbf{f}(\mathbf{r}, t) \mathbf{f}(\mathbf{r}', t') \rangle = -2\eta_0 \nabla^2 \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \mathbf{1}, \quad (2.2a)$$

with  $\mathbf{1}$  the unit tensor, as required by the fluctuation–dissipation

theorem to make the solutions to Eqs. (2.1) and (2.2) approach the correct steady-state limit at infinite time.

We suppose that in the absence of polymers the fluid is subjected to the systematic (steady) linear flow

$$\mathbf{v}_0(\mathbf{r}) = \boldsymbol{\gamma} \cdot \mathbf{r}, \quad (2.3)$$

where  $\boldsymbol{\gamma}$  is the strain-rate matrix describing the strength and pattern of the flow. Thus,  $\boldsymbol{\gamma}$  is an arbitrary traceless matrix, which is permitted in Sec. VI to become an explicit function of time. The solvent velocity is written as the unperturbed flow plus the “fluctuating portion”  $\mathbf{v}$ ,

$$\mathbf{u}(\mathbf{r}, t) = \mathbf{v}_0(\mathbf{r}) + \mathbf{v}(\mathbf{r}, t). \quad (2.4)$$

If the flow rate is sufficiently small, the convective term  $\rho_0 \mathbf{u} \cdot \nabla \mathbf{u}$  in Eq. (2.2) can be ignored to simplify that equation to

$$\begin{aligned} & \left( \rho_0 \frac{\partial}{\partial t} - \eta_0 \nabla^2 \right) \mathbf{u}(\mathbf{r}, t) + \nabla p \\ &= \mathbf{f}(\mathbf{r}, t) + \sum_{\alpha} \int d\tau_{\alpha} \delta[\mathbf{r} - \mathbf{c}_{\alpha}(\tau_{\alpha}, t)] \frac{\partial^2}{\partial \tau_{\alpha}^2} \mathbf{c}_{\alpha}(\tau_{\alpha}, t) \end{aligned} \quad (2.5)$$

for the solvent velocity field. In Eq. (2.5) and henceforth integrations over  $\tau_{\alpha}$  are implicitly understood to run from 0 to  $N_0$ .

## III. GENERAL SCHEME FOR SOLVING EQUATIONS

Our goal here is to combine Eqs. (2.1) and (2.5) and obtain an effective equation of motion for the polymer solution in which an average, described below, has been performed over the polymer degrees of freedom. We proceed by providing formal solutions to Eqs. (2.1) and (2.5). Substitution of Eqs. (2.3) and (2.4) into Eq. (2.1) allows the formal solution of the latter to be written as

$$\begin{aligned} \mathbf{c}(\tau, t) &= \mathbf{c}_0^{(0)}(\tau, t) + \int d\tau' \int d^d r' \int_{t_0}^{\infty} dt' \\ & \quad \times G_0(\tau\tau'|t-t') \delta[\mathbf{r}' - \mathbf{c}(\tau', t')] \mathbf{u}(\mathbf{r}', t'), \end{aligned} \quad (3.1)$$

$$\begin{aligned} \mathbf{c}_0^{(0)}(\tau, t) &= \int d\tau' G_0(\tau\tau'|t-t_0) \mathbf{c}(\tau') \\ & \quad + \int d\tau' \int_{t_0}^{\infty} dt' G_0(\tau\tau'|t-t') \boldsymbol{\theta}(\tau', t'), \end{aligned} \quad (3.2)$$

where  $t_0$  is some initial time in the distant past and the zero flow Green’s function  $G_0(\tau\tau'|t)$  has the Rouse mode expansion

$$\begin{aligned} G_0(\tau\tau'|t) &= \Theta(t) N_0^{-1} \left[ 1 + 2 \sum_{p=1}^{n_0-1} \cos(\hat{p}\tau) \cos(\hat{p}\tau') \exp(-t/\tau_p) \right], \end{aligned} \quad (3.3a)$$

with  $\Theta$  the step function and  $\tau_p$  the Rouse relaxation times

$$\tau_p = \xi_0 / \hat{p}^2, \quad \hat{p} = \pi p / N_0. \quad (3.3b)$$

Here  $n_0 = N_0/l$  is the total number of beads on a single polymer chain. The quantity  $\mathbf{c}(\tau')$  in Eq. (3.2) is the polymer conformation at some initial  $t = t_0$  and belongs to the equilibrium ensemble characterized by the Edwards Hamiltonian which is described in Eq. (4.5a) below.

Introducing Eq. (2.4) into (2.5) enables the formal solution of the latter to be written as

$$\mathbf{u}(\mathbf{r}, t) = \mathbf{v}_0(\mathbf{r}) + \int_{\mathbf{k}} \mathbf{T}(\mathbf{k}) \cdot \left( \sum_{\alpha} \int d\tau_{\alpha} \times \exp(-i\mathbf{k} \cdot \mathbf{c}_{\alpha}) \frac{\partial^2}{\partial \tau_{\alpha}^2} \mathbf{c}_{\alpha} + \mathbf{f}_{\mathbf{k}}(t) \right) \exp(i\mathbf{k} \cdot \mathbf{r}), \quad (3.4a)$$

where  $\int_{\mathbf{k}}$  denotes the integral  $(2\pi)^{-d} \int d^d k$ ,  $\mathbf{T}(\mathbf{k})$  is the Fourier transform of the Oseen tensor,<sup>2,6</sup>

$$\mathbf{T}(\mathbf{k}) \equiv (k^2 \eta_0)^{-1} (\mathbf{1} - \mathbf{k}\mathbf{k}/k^2) \quad (3.4b)$$

and  $\mathbf{f}_{\mathbf{k}}(t)$  is the spatial Fourier transform of  $\mathbf{f}(\mathbf{r}, t)$ . In Eqs. (3.4) and henceforth a simplified notation is adopted in which

$$\mathbf{c}_{\alpha}^{(0)} \equiv \mathbf{c}_{\alpha}^{(0)}(\tau_{\alpha}, t), \quad \mathbf{c}_{\alpha} \equiv \mathbf{c}_{\alpha}(\tau_{\alpha}, t), \quad \mathbf{c}'_{\alpha} \equiv \mathbf{c}_{\alpha}(\tau'_{\alpha}, t'), \quad \text{etc.} \quad (3.4c)$$

Inserting  $\mathbf{c}(\tau, t)$  from Eq. (3.1) into Eqs. (3.4) permits the solution (3.4) to be expressed as

$$\begin{aligned} \mathbf{u}(\mathbf{r}, t) = & \mathbf{v}_0(\mathbf{r}) + \int_{\mathbf{k}} \mathbf{T}(\mathbf{k}) \cdot \left( \sum_{\alpha} \int d\tau_{\alpha} \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{c}_{\alpha})] \frac{\partial^2}{\partial \tau_{\alpha}^2} \mathbf{c}_{0,\alpha}^{(0)} + \exp(i\mathbf{k} \cdot \mathbf{r}) \mathbf{f}_{\mathbf{k}}(t) \right) \\ & + \int d^d r' \int_{t_0}^{\infty} dt' \int_{\mathbf{k}} \mathbf{T}(\mathbf{k}) \cdot \sum_{\alpha} \int d\tau_{\alpha} \int d\tau'_{\alpha} \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{c}_{\alpha})] \\ & \times \frac{\partial^2}{\partial \tau_{\alpha}^2} G_0(\tau_{\alpha} \tau'_{\alpha} | t - t') \exp[i\mathbf{k} \cdot (\mathbf{r}' - \mathbf{c}'_{\alpha})] \mathbf{u}(\mathbf{r}', t'), \end{aligned} \quad (3.5a)$$

which may be rewritten in symbolic notation as

$$\mathbf{u} = \mathbf{v}_0 + \mathbf{v}^{(0)} + \mathbf{A} \cdot \mathbf{u}, \quad (3.5b)$$

where the initial condition-random force term is

$$\begin{aligned} \mathbf{v}^{(0)}(\mathbf{r}, t) = & \int_{\mathbf{k}} \mathbf{T}(\mathbf{k}) \cdot \left( \sum_{\alpha} \int d\tau_{\alpha} \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{c}_{\alpha})] \right. \\ & \times \left. \frac{\partial^2 \mathbf{c}_{0,\alpha}^{(0)}}{\partial \tau_{\alpha}^2} + \exp(i\mathbf{k} \cdot \mathbf{r}) \mathbf{f}_{\mathbf{k}}(t) \right), \end{aligned} \quad (3.5c)$$

and where  $\mathbf{A}$  is defined as the integral operator with kernel

$$\begin{aligned} \mathbf{A}(\mathbf{r}t | \mathbf{r}'t') = & \sum_{\alpha} \int d\tau_{\alpha} \int d\tau'_{\alpha} \int_{\mathbf{k}} \mathbf{T}(\mathbf{k}) \\ & \times \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{c}_{\alpha})] \frac{\partial^2}{\partial \tau_{\alpha}^2} G_0(\tau_{\alpha} \tau'_{\alpha} | t - t') \\ & \times \exp[i\mathbf{k} \cdot (\mathbf{r}' - \mathbf{c}'_{\alpha})] \equiv \sum_{\alpha} \mathbf{A}_{\alpha}. \end{aligned} \quad (3.6)$$

Equations (3.5) are easily solved formally to yield

$$\mathbf{u}(\mathbf{r}, t) = [\mathbf{1} - \mathbf{A}(\mathbf{r}t | \mathbf{r}'t')]^{-1} \cdot [\mathbf{v}_0(\mathbf{r}') + \mathbf{v}^{(0)}(\mathbf{r}', t')], \quad (3.7)$$

where integrations over  $\mathbf{r}'$  and  $t'$  are implicitly understood to be taken, and  $\mathbf{1}$  is both the unit operator and unit tensor.

Next we consider the force density acting on the fluid due to the polymers. Using Eq. (3.1) the force  $\mathbf{F}^p$  on the right-hand side of Eq. (2.5) becomes

$$\begin{aligned} \mathbf{F}^p(t) \equiv & \sum_{\alpha} \int d\tau_{\alpha} \delta(\mathbf{r} - \mathbf{c}_{\alpha}) \frac{\partial^2}{\partial \tau_{\alpha}^2} \mathbf{c}_{\alpha} \\ = & \mathbf{F}_0^p(t) + \int d^d r' \int_{t_0}^{\infty} dt' B(\mathbf{r}t | \mathbf{r}'t') \mathbf{u}(\mathbf{r}', t'), \end{aligned} \quad (3.8)$$

where the first term  $\mathbf{F}_0^p$  is given by

$$\mathbf{F}_0^p = \sum_{\alpha} \int d\tau_{\alpha} \delta(\mathbf{r} - \mathbf{c}_{\alpha}) \frac{\partial^2}{\partial \tau_{\alpha}^2} \mathbf{c}_{0,\alpha}^{(0)} \equiv \sum_{\alpha} \mathbf{F}_{0,\alpha}^p, \quad (3.9)$$

and where the scattering function  $B$  is defined by

$$\begin{aligned} B(\mathbf{r}t | \mathbf{r}'t') = & \sum_{\alpha} \int d\tau_{\alpha} \int d\tau'_{\alpha} \delta(\mathbf{r} - \mathbf{c}_{\alpha}) \frac{\partial^2}{\partial \tau_{\alpha}^2} \\ & \times G_0(\tau_{\alpha} \tau'_{\alpha} | t - t') \delta(\mathbf{r}' - \mathbf{c}'_{\alpha}) \\ \equiv & \sum_{\alpha} B_{\alpha}. \end{aligned} \quad (3.10)$$

Both  $\mathbf{A}$  of Eq. (3.6) and  $B$  of Eq. (3.10) are functions of the polymer configuration at a pair of times; hence, they depend on the polymer dynamics.

As mentioned above, we are interested in the average properties of the polymer solution when an average is performed over a distribution of the conformations of the polymer chains at some initial time  $t_0$ . We may obtain the averaged equation of motion for the polymer solution by expressing the conformational average of  $\mathbf{F}^p(t)$  in terms of the average of  $\mathbf{u}(\mathbf{r}, t)$ . We begin this process by evaluating the average of  $\mathbf{F}^p$  of Eq. (3.8) over polymer conformations at some initial time  $t_0$  in the distant past where the polymer solution is assumed to be at rest and in equilibrium. An average is also performed over the random forces according to Eqs. (2.1a) and (2.1b). Denote the averaged quantities by  $\langle \mathbf{F}^p \rangle$  and  $\langle \mathbf{u} \rangle$ . Combining Eqs. (3.7) and (3.8) produces the formal results

$$\begin{aligned} \langle \mathbf{F}^p \rangle = & \langle \mathbf{F}_0^p \rangle + \left\langle \sum_{\alpha} B_{\alpha} \left( \mathbf{1} - \sum_{\beta} \mathbf{A}_{\beta} \right)^{-1} \right\rangle \cdot \mathbf{v}_0 \\ & + \left\langle \sum_{\alpha} B_{\alpha} \left( \mathbf{1} - \sum_{\beta} \mathbf{A}_{\beta} \right)^{-1} \cdot \mathbf{v}^{(0)} \right\rangle, \end{aligned} \quad (3.11a)$$

$$\langle \mathbf{u} \rangle = \left\langle \left( \mathbf{1} - \sum_{\alpha} \mathbf{A}_{\alpha} \right)^{-1} \right\rangle \cdot \mathbf{v}_0 + \left\langle \left( \mathbf{1} - \sum_{\alpha} \mathbf{A}_{\alpha} \right)^{-1} \cdot \mathbf{v}^{(0)} \right\rangle, \quad (3.11b)$$

where the first equation is obtained by averaging over Eq. (3.8) for  $\mathbf{F}^p$  and by using Eq. (3.7). The second equation follows from averaging Eq. (3.7) for  $\mathbf{u}$ . Now elimination of  $\mathbf{v}_0$  between the two equations in Eq. (3.11) produces the final expression for  $\langle \mathbf{F}^p \rangle$  and the corresponding averaged equation of Eq. (2.5) as

$$\left(\rho_0 \frac{\partial}{\partial t} - \eta_0 \nabla^2\right) \langle \mathbf{u} \rangle + \nabla \langle p \rangle = \langle \mathbf{F}^p \rangle, \quad (3.12a)$$

where the averaged polymer force density is formally obtained as

$$\begin{aligned} \langle \mathbf{F}^p \rangle = & \langle \mathbf{F}_0^p \rangle + \left\langle \sum_{\alpha} B_{\alpha} \left( \mathbf{1} - \sum_{\beta} A_{\beta} \right)^{-1} \right. \\ & \cdot \left\langle \left( \mathbf{1} - \sum_{\gamma} A_{\gamma} \right)^{-1} \right\rangle^{-1} \cdot \langle \mathbf{u} \rangle \\ & + \left\langle \sum_{\alpha} B_{\alpha} \left( \mathbf{1} - \sum_{\beta} A_{\beta} \right)^{-1} \cdot \mathbf{v}^{(0)} \right\rangle \\ & - \left\langle \sum_{\alpha} B_{\alpha} \left( \mathbf{1} - \sum_{\beta} A_{\beta} \right)^{-1} \right\rangle \cdot \left\langle \left( \mathbf{1} - \sum_{\gamma} A_{\gamma} \right)^{-1} \right\rangle^{-1} \\ & \cdot \left\langle \left( \mathbf{1} - \sum_{\mu} A_{\mu} \right)^{-1} \cdot \mathbf{v}^{(0)} \right\rangle. \end{aligned} \quad (3.12b)$$

Equations (3.12) provide the general formal solution that is used to investigate the viscoelastic properties of the polymeric fluid over *all* concentration ranges for which macroscopic manifestations of entanglements, such as the 3.4 power law for the viscosity, are absent and for which the volume fraction of polymers is sufficiently low.

Henceforth, we simplify Eqs. (3.12) by considering the important limit of infinite dilution. To first order in concentration  $c$ , the double sums in Eq. (3.12b) become single sums and the sums over  $\gamma$  and  $\mu$  are dropped because they only contribute at order  $c^2$ . Thus, Eq. (3.12b) reduces in infinite dilution to

$$\begin{aligned} \langle \mathbf{F}^p \rangle = & \langle \mathbf{F}_0^p \rangle + \sum_{\alpha} \langle B_{\alpha} (\mathbf{1} - A_{\alpha})^{-1} \rangle \cdot \langle \mathbf{u} \rangle \\ & + \sum_{\alpha} \langle B_{\alpha} (\mathbf{1} - A_{\alpha})^{-1} \cdot \mathbf{v}^{(0)} \rangle. \end{aligned} \quad (3.13)$$

It is straightforward to show that the first and third terms of the right-hand side of Eq. (3.13) are zero. (See the Appendix.) Consequently, the insertion of Eq. (3.13) into the averaged Navier–Stokes equation (3.12a) produces the effective Navier–Stokes equation for the averaged polymer solution velocity field

$$\left(\rho_0 \frac{\partial}{\partial t} - \eta_0 \nabla^2\right) \langle \mathbf{u} \rangle + \nabla \langle p \rangle = \sum_{\alpha} \langle B_{\alpha} (\mathbf{1} - A_{\alpha})^{-1} \rangle \cdot \langle \mathbf{u} \rangle, \quad (3.14)$$

where  $B_{\alpha}$  and  $A_{\alpha}$  are defined in Eqs. (3.10) and (3.6). Equation (3.14) represents the starting equation for the study of the low frequency hydrodynamics of polymer–flow interactions in dilute solutions. Our interest here lies in using Eq. (3.14) to investigate the viscoelastic properties of the polymer solution in order to examine the non-Newtonian behaviors observed experimentally.<sup>4</sup> However, it should be cautioned that Eq. (3.14) is valid only for dilute polymer solutions, for low frequencies where the solvent hydrodynamic is adequately described using the static Oseen tensor and for flow rates low enough that the fluid convection term  $\rho_0 \mathbf{u} \cdot \nabla \mathbf{u}$  in Eq. (2.2) can be neglected. Extensions to include fluid dynamics and convection are left for future work.

#### IV. ROUSE CHAIN HYDRODYNAMICS

This section specializes to the simplest Rouse limit where complications due to the solvent mediated hydrodynamic interactions among polymer beads are omitted. The Rouse limit is of importance because it permits us to derive an exact solution of the model and thereby provide the first Langevin chainlike molecule based theoretical insight into the effective hydrodynamics of polymer solutions under flow. Moreover, this Rouse limit is also the lowest order calculation in a more thorough renormalization group treatment of the non-Newtonian behavior of polymer solutions within the present kinetic model for the low frequency dynamics of polymer solutions under flow.

We begin our investigation of the Rouse hydrodynamics by reducing the general results of Sec. III to this limit, retaining contributions that are zeroth order in the Oseen tensor  $\mathbf{T}(\mathbf{k})$ . This limit corresponds to dropping  $A_{\alpha}$  in Eq. (3.14). Hence, the Rouse limit of Eq. (3.14) is written symbolically as

$$\left(\rho_0 \frac{\partial}{\partial t} - \eta_0 \nabla^2\right) \langle \mathbf{u} \rangle + \nabla \langle p \rangle = \sum_{\alpha} \langle B_{\alpha} \rangle \langle \mathbf{u} \rangle, \quad (4.1)$$

where the solution to Eq. (2.1) for the polymer configurations in the *Rouse limit* may alternatively be represented in the convenient form

$$\begin{aligned} \mathbf{c}(\tau, t) \rightarrow \mathbf{c}^{(0)}(\tau, t) \\ = \int d\tau' G(\tau\tau'|t - t_0) \cdot \mathbf{c}(\tau') \\ + \int d\tau' \int_{t_0}^{\infty} dt' G(\tau\tau'|t - t') \cdot \boldsymbol{\theta}(\tau', t'), \end{aligned} \quad (4.1a)$$

with the flow dependent Green's function given by

$$G(\tau\tau'|t) = \exp(\gamma t) G_0(\tau\tau'|t). \quad (4.1b)$$

Let  $\mathbf{R}(\tau)$  denote the initial position of the polymer bead at  $\tau$  with respect to the polymer's center of mass at  $\mathbf{c}_0$ . Then  $\mathbf{c}^{(0)}(\tau, t)$  of Eq. (4.1a) becomes

$$\begin{aligned} \mathbf{c}(\tau, t) \rightarrow \mathbf{c}^{(0)}(\tau, t) = \exp[\gamma(t - t_0)] \cdot \mathbf{c}_0 \\ + \int d\tau_1 G(\tau\tau_1|t - t_0) \cdot \mathbf{R}(\tau_1) \\ + \int d\tau_1 \int_{t_0}^{\infty} dt_1 G(\tau\tau_1|t - t_1) \cdot \boldsymbol{\theta}(\tau_1, t_1), \end{aligned} \quad (4.2)$$

where the first term arises from the center-of-mass dynamics in which  $\mathbf{c}_0$  corresponds to the initial position of the center of mass at  $t = t_0$ . Equations (4.1) and (3.10) are the equations to be solved in the Rouse limit.

A key quantity required in solving these equations is the dynamical bead–bead single-chain scattering factor,

$$S(\mathbf{k}, \mathbf{k}'|t, t') = \langle \exp[i\mathbf{k} \cdot \mathbf{c}^{(0)}(\tau, t) + i\mathbf{k}' \cdot \mathbf{c}^{(0)}(\tau', t')] \rangle, \quad (4.3)$$

where  $\langle \rangle$  represents an average over the random forces and over the polymer conformation at time  $t_0$ , i.e., an average over the initial center-of-mass position  $\mathbf{c}_0$ , over the initial polymer conformation  $\{\mathbf{R}(\tau)\}$ , and over the random force  $\{\boldsymbol{\theta}(\tau, t)\}$ . Thus, Eq. (4.3) is reexpressed using Eq. (4.2) as

$$\begin{aligned}
S(\mathbf{k}, \mathbf{k}' | t, t') &= V^{-1} \delta[\mathbf{k} \cdot \exp[\gamma(t - t_0)] + \mathbf{k}' \cdot \exp[\gamma(t' - t_0)]] \\
&\times \left\langle \exp \left( i \mathbf{k} \cdot \exp[\gamma(t - t_0)] \int d\tau_1 Q(\tau_1 | \tau t, \tau' t') \cdot \mathbf{R}(\tau_1) \right) \right\rangle_{\mathbf{R}} \\
&\times \left\langle \exp \left( i \mathbf{k}' \cdot \exp[\gamma(t' - t_0)] \int d\tau_1 \int_{t_0}^{\infty} dt_1 \exp[\gamma \cdot (t - t_1)] [G_0(\tau \tau_1 | t - t_1) - G_0(\tau \tau_1 | t' - t_1)] \cdot \boldsymbol{\theta}(\tau_1, t_1) \right) \right\rangle_{\boldsymbol{\theta}}, \quad (4.4)
\end{aligned}$$

where  $V$  is the volume of the polymer-flow system, the delta function arises from the average over center-of-mass position  $\mathbf{c}_0$  at  $t_0$ , and  $Q$  is defined below. The Gaussian distributions for  $\{\mathbf{R}(\tau)\}$  and  $\{\boldsymbol{\theta}(\tau, t)\}$  are given, respectively, by

$$P\{\mathbf{R}\} = \exp \left[ - \left( \frac{1}{2} \right) \int d\tau \left| \frac{d\mathbf{R}(\tau)}{d\tau} \right|^2 \right] \int D\{\mathbf{R}\} \exp \left[ - \left( \frac{1}{2} \right) \int d\tau \left| \frac{d\mathbf{R}(\tau)}{d\tau} \right|^2 \right] \quad (4.5a)$$

and

$$P\{\boldsymbol{\theta}\} = \left( \frac{\xi_0}{\pi} \right)^{3/2} \exp \left[ - \left( \frac{\xi_0}{4} \right) \int d\tau \int_{-\infty}^{\infty} dt \boldsymbol{\theta}(\tau, t) \cdot \boldsymbol{\theta}(\tau, t) \right], \quad (4.5b)$$

where the argument of the exponential function in Eq. (4.5a) is called the Edwards' Hamiltonian for Gaussian chains.<sup>16</sup> Equation (4.5) enables the two averages in Eq. (4.4) to be readily performed, yielding

$$\begin{aligned}
S(\mathbf{k}, \mathbf{k}' | t, t') &= V^{-1} \delta[\mathbf{k} \cdot \exp[\gamma(t - t_0)] + \mathbf{k}' \cdot \exp[\gamma(t' - t_0)]] \exp \left( - |\mathbf{k} \cdot \exp[\gamma(t - t_0)]|^2 \right) \\
&\times \int d\tau_1 \int d\tau_2 \sum_{p=1}^{n_0-1} \frac{2}{N_0} (2\hat{p}^2)^{-1} Q(\tau_1 | \tau t, \tau' t') Q(\tau_2 | \tau t, \tau' t') \cos(\hat{p}\tau_1) \cos(\hat{p}\tau_2) \\
&\times \exp \left( - \xi_0^{-1} \int d\tau_1 \int_{t_0}^{t'} dt_1 |\mathbf{k} \cdot \exp[\gamma(t - t_1)]|^2 Q^2(\tau_1 t_1 | \tau t, \tau' t') \right. \\
&\quad \left. - \xi_0^{-1} \int d\tau_1 \int_{t'}^t dt_1 |\mathbf{k} \cdot \exp[\gamma(t - t_1)]|^2 G_0^2(\tau \tau_1 | t - t_1) \right), \quad (4.6)
\end{aligned}$$

where the  $Q$ 's are defined as

$$Q(\tau_1 | \tau t, \tau' t') = (2/N_0) \sum_{p=1}^{n_0-1} \exp(t_0/\tau_p) \cos(\hat{p}\tau_1) [\exp(-t/\tau_p) \cos(\hat{p}\tau) - \exp(-t'/\tau_p) \cos(\hat{p}\tau')], \quad (4.7a)$$

$$Q(\tau_1 t_1 | \tau t, \tau' t') = (2/N_0) \sum_{p=1}^{n_0-1} \exp(t_1/\tau_p) \cos(\hat{p}\tau_1) [\exp(-t/\tau_p) \cos(\hat{p}\tau) - \exp(-t'/\tau_p) \cos(\hat{p}\tau')]. \quad (4.7b)$$

The  $d\tau_1 d\tau_2$  integrations along the chain contour in the exponential factor of Eq. (4.6) are readily evaluated to produce

$$S(\mathbf{k}, \mathbf{k}' | t, t') = V^{-1} \delta[\mathbf{k} \cdot \exp[\gamma(t - t_0)] + \mathbf{k}' \cdot \exp[\gamma(t' - t_0)]] \exp(-\phi_{\mathbf{R}} - \phi_{\boldsymbol{\theta}}), \quad (4.8)$$

where  $\phi_{\mathbf{R}}$  and  $\phi_{\boldsymbol{\theta}}$  are given, respectively, by

$$\begin{aligned}
\phi_{\mathbf{R}}(\mathbf{k} | \tau t, \tau' t') &= |\mathbf{k} \cdot \exp[\gamma(t - t_0)]|^2 (2/N_0) \sum_{p=1}^{n_0-1} (2\hat{p}^2)^{-1} \exp(2t_0/\tau_p) \\
&\times [\exp(-t/\tau_p) \cos(\hat{p}\tau) - \exp(-t'/\tau_p) \cos(\hat{p}\tau')]^2, \quad (4.9)
\end{aligned}$$

$$\begin{aligned}
\phi_{\boldsymbol{\theta}}(\mathbf{k} | \tau t, \tau' t') &= \xi_0^{-1} (2/N_0) \int_{t_0}^{t'} dt_1 |\mathbf{k} \cdot \exp[\gamma(t - t_1)]|^2 \sum_{p=1}^{n_0-1} \exp(2t_1/\tau_p) \\
&\times [\exp(-t/\tau_p) \cos(\hat{p}\tau) - \exp(-t'/\tau_p) \cos(\hat{p}\tau')]^2 \\
&+ \xi_0^{-1} (2/N_0) \int_{t'}^t dt_1 |\mathbf{k} \cdot \exp[\gamma(t - t_1)]|^2 \left\{ \frac{1}{2} + \sum_{p=1}^{n_0-1} \exp[2(t_1 - t)/\tau_p] \cos^2(\hat{p}\tau) \right\}, \quad (4.10)
\end{aligned}$$

with the subscripts  $\mathbf{R}$  and  $\boldsymbol{\theta}$  corresponding to the contributions in Eq. (4.4) from averages over  $\mathbf{R}$  and  $\boldsymbol{\theta}$ , respectively. The quadratic dependence of  $\phi_{\mathbf{R}}$  and  $\phi_{\boldsymbol{\theta}}$  on the wave number  $\mathbf{k}$  is an important feature which is exploited in Sec. V. Throughout the calculation, the full dependence on the

strain rate, as characterized by the matrix  $\gamma$ , has been retained.

Now that the interbead dynamic scattering factor  $S$  has been evaluated in Eqs. (4.8)–(4.10), these results can be combined with Eq. (3.10) for  $B_{\alpha}$  to compute an explicit

representation for the right-hand side of Eq. (4.1). Thus, we have

$$\begin{aligned} & \langle B(\mathbf{r}t | \mathbf{r}'t') \rangle \\ &= \rho_p \int d\tau \int d\tau' \frac{\partial^2}{\partial \tau'^2} G_0(\tau\tau' | t - t') \\ & \quad \times \int_{\mathbf{k}} \int_{\mathbf{k}'} \delta\{\mathbf{k} \cdot \exp[\gamma(t - t_0)] + \mathbf{k}' \cdot \exp[\gamma(t' - t_0)]\} \\ & \quad \times \exp(-i\mathbf{k} \cdot \mathbf{r} - i\mathbf{k}' \cdot \mathbf{r}') \\ & \quad \times \exp[-\phi_{\mathbf{R}}(\mathbf{k} | \tau t, \tau' t) - \phi_{\mathbf{\theta}}(\mathbf{k} | \tau t, \tau' t')], \quad (4.11) \end{aligned}$$

where  $\rho_p = n_p/V$  is the polymer chain number density. The combination of Eqs. (4.1) and (4.11) provides the exact solution for the hydrodynamics of a dilute solution of Rouse chains in an arbitrary linear flow field. To proceed further with Eq. (4.11), the next section studies the long wavelength  $\mathbf{k} \rightarrow 0$  hydrodynamic limit of the effective Navier-Stokes equation for the averaged solution velocity field as defined by the combination of Eqs. (4.1) and (4.11).

## V. LONG WAVELENGTH LIMIT AND CONSTITUTIVE EQUATION

The Rouse limit solution in the previous section applies to the hydrodynamical properties of the polymer solution on all length scales, including those comparable to chain dimensions. While hydrodynamics on these smaller length scales is of relevance in understanding phenomena loosely associated with the term microscopic viscosity, the central interest in rheology lies in the properties of the polymer solution velocity field at long wavelengths. Hence, we now further specialize to the long wavelength Rouse limit hydrodynamics where it proves possible to evaluate all the integrals to provide an exact closed form solution for the linear flow of Eq. (2.3).

Begin by taking the spatial Fourier transform of the both sides in the combination of Eqs. (4.1) and (4.11). Passing to the long wavelength limit implies the expansion of Eq. (4.11) to leading order in  $\phi_{\mathbf{R}}$  and  $\phi_{\mathbf{\theta}}$  (order  $k^2$ ). Thus, the effective hydrodynamic equation of motion in Fourier space in the limit of very small wave numbers  $\mathbf{k}$  becomes

$$\begin{aligned} & \left( \rho_0 \frac{\partial}{\partial t} + \eta_0 k^2 \right) \mathbf{u}_{\mathbf{k}}(t) + i\mathbf{k}p \\ &= -\rho_p \int d\tau \int d\tau' \int_{t_0}^t dt' \frac{\partial^2}{\partial \tau'^2} G_0(\tau\tau' | t - t') \\ & \quad \times \int_{\mathbf{k}'} \mathbf{u}_{\mathbf{k}'}(t') \delta\{\mathbf{k} \cdot \exp[\gamma(t' - t_0)] \\ & \quad - \mathbf{k}' \cdot \exp[\gamma(t - t_0)]\} \\ & \quad \times [\phi_{\mathbf{R}}(\mathbf{k} | \tau t, \tau' t') + \phi_{\mathbf{\theta}}(\mathbf{k} | \tau t, \tau' t')], \quad (5.1) \end{aligned}$$

where terms of higher order in  $k^2$  are neglected on the right-hand side and the brackets  $\langle \rangle$  are omitted on u.

Substitute Eqs. (4.9) and (4.10) into Eq. (5.1) and then integrate the right-hand side of the latter over  $\tau$  and  $\tau'$ . These operations convert Eq. (5.1) to

$$\begin{aligned} & \left( \rho_0 \frac{\partial}{\partial t} + \eta_0 k^2 \right) \mathbf{u}_{\mathbf{k}}(t) + i\mathbf{k}p \\ &= -\rho_p \int_{t_0}^t dt' \int_{\mathbf{k}'} \mathbf{u}_{\mathbf{k}'}(t') \delta\{\mathbf{k} \cdot \exp[\gamma(t' - t_0)] \\ & \quad - \mathbf{k}' \cdot \exp[\gamma(t - t_0)]\} \sum_{p=1}^{n_0-1} \exp(-2t/\tau_p) \\ & \quad \times \left[ \exp(2t_0/\tau_p) |\mathbf{k} \cdot \exp[\gamma(t - t_0)]|^2 \right. \\ & \quad \left. + \int_{t_0}^{t'} dt_1 (2/\tau_p) |\mathbf{k} \cdot \exp[\gamma(t - t_1)]|^2 \exp(2t_1/\tau_p) \right]. \quad (5.2) \end{aligned}$$

Equation (5.2) describes the long wavelength behavior of dilute polymer solutions under an *arbitrary* systematic *linear* flow in the range of sufficiently low flow rates where the convective term of the Navier-Stokes equation is unimportant.

The general equation (5.2) is further illustrated by specializing to some experimentally well studied three-dimensional linear flows. This requires explicit expressions for the vector  $\mathbf{k} \cdot \exp(\alpha\gamma)$  and scalar  $|\mathbf{k} \cdot \exp(\alpha\gamma)|^2$ . Planar or simple elongational flows have the strain rate matrix,

$$\gamma = \begin{pmatrix} \dot{\gamma}_{11} & 0 & 0 \\ 0 & \dot{\gamma}_{22} & 0 \\ 0 & 0 & \dot{\gamma}_{33} \end{pmatrix}, \quad (5.3)$$

which has the property

$$[\exp(\alpha\gamma)]_{ij} = \delta_{ij} \exp(\alpha\dot{\gamma}_{ii}), \quad (5.4a)$$

and, consequently, it is readily found that

$$\mathbf{k} \cdot \exp(\alpha\gamma) = \sum_{i=1}^3 \mathbf{e}_i k_i \exp(\alpha\dot{\gamma}_{ii}), \quad (5.4b)$$

$$|\mathbf{k} \cdot \exp(\alpha\gamma)|^2 = \sum_{i=1}^3 k_i^2 \exp(2\alpha\dot{\gamma}_{ii}), \quad (5.4c)$$

where  $\mathbf{e}_i$  is a unit vector in the  $i$ th Cartesian direction, and  $k_i$  is the  $i$ th component of  $\mathbf{k}$ .

Simple shear flow has the strain rate matrix

$$\gamma = \begin{pmatrix} 0 & \dot{\gamma}_{12} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (5.5a)$$

which possesses the special property

$$\exp(\alpha\gamma) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \alpha\dot{\gamma}_{12} \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (5.5b)$$

Straightforward computations in this case yield

$$\mathbf{k} \cdot \exp(\alpha\gamma) = \mathbf{e}_1 k_1 + \mathbf{e}_2 (k_2 + \alpha\dot{\gamma}_{12} k_1) + \mathbf{e}_3 k_3, \quad (5.5c)$$

$$|\mathbf{k} \cdot \exp(\alpha\gamma)|^2 = k_1^2 + (k_2 + \alpha\dot{\gamma}_{12} k_1)^2 + k_3^2. \quad (5.5d)$$

Now we perform integrations over  $\mathbf{k}'$  and  $t_1$  on the right-hand side of Eq. (5.2) for each of the two types of flow discussed above.

After some straightforward integrations, the right-hand side of Eq. (5.2), written as  $\langle \mathbf{F}_{\mathbf{k}}^p(t) \rangle$ , can be reduced for the elongational flow of Eq. (5.3) to

$$\begin{aligned} \langle \mathbf{F}_k^p(t) \rangle = & -\rho_p \int_{t_0}^t dt' \mathbf{u}_k(t') \sum_{p=1}^{n_0-1} \exp(-2t/\tau_p) \\ & \times \sum_{i=1}^3 k_i^2 (1 - \dot{\gamma}_{ii} \tau_p)^{-1} \{ \exp(2t'/\tau_p) \\ & \times \exp[2(t-t')\dot{\gamma}_{ii}] \\ & - (\dot{\gamma}_{ii} \tau_p) \exp[2t_0(1 - \dot{\gamma}_{ii} \tau_p)/\tau_p] \}, \quad (5.6) \end{aligned}$$

where throughout the remainder of this section  $\mathbf{k}'$  designates

$$\mathbf{k}' \equiv \mathbf{k} \cdot \exp[\boldsymbol{\gamma}(t-t')]. \quad (5.6a)$$

The expression for simple shear flows is also readily obtained and is presented below.

Substitution of Eq. (5.6) into Eq. (5.2) produces the dilute solution Rouse limit elongational flow hydrodynamic equation as

$$\begin{aligned} \left( \rho_0 \frac{\partial}{\partial t} + \eta_0 k^2 \right) \mathbf{u}_k(t) + i\mathbf{k}p \\ = -\rho_p \int_{t_0}^t dt' \mathbf{u}_k(t') \sum_{p=1}^{n_0-1} \exp(-2t/\tau_p) \\ \times \sum_{i=1}^3 k_i^2 (1 - \dot{\gamma}_{ii} \tau_p)^{-1} \\ \times \{ \exp(2t'/\tau_p) \exp[2\dot{\gamma}_{ii}(t-t')] - (\dot{\gamma}_{ii} \tau_p) \\ \times \exp[2t_0(1 - \dot{\gamma}_{ii} \tau_p)/\tau_p] \} \quad (5.7) \end{aligned}$$

for the fluid velocity field  $\mathbf{u}$ . Equation (5.7) has been derived from first principles within a well defined, albeit in some ways simplified chainlike model. This equation is in a form which is similar to a many relaxation time generalization of nonlinear models of continuum mechanics.<sup>4</sup> Popular dumbbell models yield a single relaxation time, and the presence of many relaxation times in Eq. (5.7) is quite natural. It is possible to consider more sophisticated models by relaxing some of the assumptions of the steady state hydrodynamics Rouse model used here. However, the technical difficulties become severe.

The second term in Eq. (5.7) contains the initial time  $t_0$  and represents a contribution from the transients that appear in our effective hydrodynamic equation because of our assumption that the polymers are at equilibrium at this initial time. Setting  $t_0 = -\infty$  yields the steady-state limit which is generally of interest in experiments. Thus, the steady-flow limit of Eq. (5.7) becomes

$$\begin{aligned} \left( \rho_0 \frac{\partial}{\partial t} + \eta_0 k^2 \right) \mathbf{u}_k(t) + i\mathbf{k}p \\ = -\rho_p \int_{-\infty}^t dt' \mathbf{u}_k(t') \\ \times \sum_{p=1}^{n_0-1} \exp\left(\frac{-2(t-t')}{\tau_p}\right) \sum_{i=1}^3 k_i^2 (1 - \dot{\gamma}_{ii} \tau_p)^{-1}, \quad (5.8) \end{aligned}$$

and is derived under the condition  $\dot{\gamma}_{ii} \tau_p < 1$  for any  $i$  and  $p$ . Our Gaussian model becomes inadequate for  $\dot{\gamma}_i \tau_p \geq 1$  as the condition  $\dot{\gamma}_{11} \tau_1 \approx 1$  roughly corresponds to the onset of the coil-stretch transition. The term on the right-hand side of Eq. (5.8) is not isotropic in  $\mathbf{k}$  space because the  $\dot{\gamma}_{ii}$ 's are unequal and the different spatial directions have different overall amplitudes  $(1 - \dot{\gamma}_{ii} \tau_p)^{-1}$ . This feature is reflected in

the specific form of the averaged polymer solution stress tensor  $\Pi$ , which we derive below.

The corresponding steady-state limit of the hydrodynamic equation for the simple flow of Eq. (5.5a) follows readily from Eq. (5.2). Using Eqs. (5.5c) and (5.5d) to perform the integrations over  $t_1$  and  $\mathbf{k}'$  in Eq. (5.2), we find

$$\begin{aligned} \left( \rho_0 \frac{\partial}{\partial t} + \eta_0 k^2 \right) \mathbf{u}_k(t) + i\mathbf{k}p \\ = -\rho_p \int_{-\infty}^t dt' \mathbf{u}_k(t') \sum_{p=1}^{n_0-1} \exp(-2(t-t')/\tau_p) \\ \times \{ k_1'^2 [1 + (\dot{\gamma}_{12} \tau_p/2)^2] \\ + [k_2'^2 + k_1'(\dot{\gamma}_{12} \tau_p/2)]^2 + k_3'^2 \} \quad (5.9) \end{aligned}$$

in the steady-state limit (obtained by setting  $t_0 = -\infty$  to eliminate transients). In contrast to Eq. (5.8), the derivation of Eq. (5.9) does not require the constraint  $\dot{\gamma}_{12} \tau_p < 1$ . As is well known, this is because shear flows do not stretch polymer chains as strongly as do elongational flows. Hence, simple shear flows do not produce in the Rouse model the coil-stretch transition at which the Gaussian chain model becomes inapplicable. On the other hand, Eq. (5.9) is valid only for weak flows for which the convection term is negligible. Another special feature of shear flows is that the shear flow only generates weak nonlinearities in the Rouse model. No terms of higher order in  $\dot{\gamma}_{12}$  than  $(\dot{\gamma}_{12})^2$  are present in Eq. (5.9), but the introduction of hydrodynamic interactions may lead the  $\tau_p$  to depend on  $\dot{\gamma}_{12}$  to give strong nonlinearities again.

A central quantity in the study of non-Newtonian fluid mechanics is the constitutive equation relating the stress tensor  $\Pi$  to the strain rate tensor  $\dot{\boldsymbol{\gamma}}$ . A majority of previous works postulate phenomenological constitutive equations, while a few molecular treatments have been performed using dumbbell models.<sup>4</sup> Our analysis of the Rouse limits in Eqs. (5.8) and (5.9) now permit us to extract the dilute solution Rouse model  $\Pi$  in arbitrary linear flows.

Let  $\Pi_k(t)$  be the spatial Fourier transform of  $\Pi(\mathbf{r}, t)$ . The Navier-Stokes equation for the averaged polymer solution is written in terms of  $\Pi_k(t)$  as

$$\rho_0 \frac{\partial}{\partial t} \mathbf{u}_k(t) + i\mathbf{k} \cdot \Pi_k(t) = 0. \quad (5.10)$$

A comparison of Eq. (5.8) or (5.9) with (5.10) enables the stress tensor to be determined. The calculation uses the fact that to zeroth order in the hydrodynamic interactions the  $\mathbf{u}_k$  in Eqs. (5.8) and (5.9) may be replaced by the unperturbed  $\mathbf{v}_k^0$  in performing the calculations. At the end  $\mathbf{u}_k$  may be restored, again consistent with the order of the approximation. The symmetric dilute solution Rouse model stress tensor then emerges in the general form.

$$\begin{aligned} \Pi_k(t) = & p\mathbf{1} - \eta_0 [ (i\mathbf{k}) \mathbf{u}_k(t) + \mathbf{u}_k(t) (i\mathbf{k}) ] \\ & - \rho_p \int_{-\infty}^t dt' \sum_{p=1}^{n_0-1} \exp(-2(t-t')/\tau_p) \\ & \times [ \mathbf{J}_p(t-t') \cdot (i\mathbf{k}) \mathbf{u}_k(t') \\ & + \mathbf{u}_k(t') \mathbf{J}_p(t-t') \cdot (i\mathbf{k}) ], \quad (5.11) \end{aligned}$$

where the last term in  $\mathbf{v}_k^0 \mathbf{J}_p \cdot (i\mathbf{k})$  is absent for elongational



flows as the first factor in the square brackets is already symmetric. The tensor  $J_p(t-t')$  is written as

$$J_p(t-t') = \exp[\gamma(t-t')] \cdot J_p \cdot \exp[\gamma^T(t-t')], \quad (5.11a)$$

where the tensor  $J_p$  has the matrix representation

$$J_p = \begin{pmatrix} (1 - \dot{\gamma}_{11}\tau_p)^{-1} & 0 & 0 \\ 0 & (1 - \dot{\gamma}_{22}\tau_p)^{-1} & 0 \\ 0 & 0 & (1 - \dot{\gamma}_{33}\tau_p)^{-1} \end{pmatrix}, \quad (5.12)$$

and where the incompressibility constraint  $\mathbf{k} \cdot \mathbf{u}_\mathbf{k} = 0$  is used for shear to express Eq. (5.11) in a symmetric form. Transforming  $\Pi$  to coordinate space gives

$$\begin{aligned} \Pi(\mathbf{r}, t) = & p\mathbf{1} - \eta_0[\nabla\mathbf{u}(\mathbf{r}, t) + (\nabla\mathbf{u})^T] \\ & - \rho_p \int_{-\infty}^t dt' \sum_{p=1}^{n_0-1} \exp[-2(t-t')/\tau_p] \\ & \times [J_p \cdot \nabla\mathbf{u}(\mathbf{r}', t') + (J_p \cdot \nabla\mathbf{u})^T], \end{aligned} \quad (5.13)$$

where  $\mathbf{r}' = \exp[-\gamma(t-t')] \cdot \mathbf{r}$  and the last factor is again absent for elongational flow.

The combination of Eqs. (5.9) and (5.10), on the other hand, yields the symmetric dilute solution Rouse model stress tensor  $\Pi$  for the deterministic simple shear flow of Eq. (5.5). The shear flow stress tensor is identical in form to Eqs. (5.11) and (5.13), except that the diagonal matrix  $J_p$  in Eq. (5.12) is replaced by the nondiagonal symmetric

$$J'_p = \begin{pmatrix} 1 + 2(\dot{\gamma}_{12}\tau_p/2)^2 & \dot{\gamma}_{12}\tau_p/2 & 0 \\ \dot{\gamma}_{12}\tau_p/2 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (5.14)$$

Equation (5.13) or (5.11), together with Eqs. (5.12) and (5.14) represent the main results of this paper. Our approach and its extensions now permit the first principles microscopic derivation of constitutive equations for polymer solutions under flow.

## VI. NONSTATIONARY FLOWS AND MATERIAL FUNCTIONS

While the calculations in Secs. III–V treat  $\gamma$  as time independent, the dynamical case proceeds by the replacement of  $\gamma(t_1 - t_2)$  in  $G$  of Eq. (4.1b) by  $\int_{t_1}^{t_2} \gamma(t') dt'$ . This replacement merely converts all the factors of  $\gamma(t_1 - t_2)$  in Eq. (5.2) into  $\int_{t_1}^{t_2} \gamma(t') dt'$ . The integration over  $\mathbf{k}'$  in Eq. (5.2) may be performed for elongational and simple shear flows to yield, respectively,

$$\begin{aligned} \langle F_k^p(t) \rangle_{\text{elongation}} = & -\rho_p \int_{-\infty}^t dt' \mathbf{u}_{\mathbf{k}'}(t') \sum_{p=1}^{n_0-1} \exp(-2t/\tau_p) \\ & \times \int_{-\infty}^{t'} dt_1 (2/\tau_p) \exp(2t_1/\tau_p) \sum_{i=1}^3 k_i'^2 \\ & \times \exp\left(2 \int_{t_1}^{t'} dt_2 \dot{\gamma}_{ii}(t_2)\right), \end{aligned} \quad (6.1)$$

$$\begin{aligned} \langle F_k^p(t) \rangle_{\text{shear}} = & -\rho_p \int_{-\infty}^t dt' \mathbf{u}_{\mathbf{k}'}(t') \sum_{p=1}^{n_0-1} \exp(-2t/\tau_p) \\ & \times \int_{-\infty}^{t'} dt_1 (2/\tau_p) \exp(2t_1/\tau_p) \\ & \times \left[ k_1'^2 + \left( k_1' \int_{t_1}^{t'} dt_2 \dot{\gamma}_{12}(t_2) + k_2' \right)^2 + k_3'^2 \right], \end{aligned} \quad (6.2)$$

where  $\mathbf{k}'$  is given in this section by  $\mathbf{k}' = \mathbf{k} \cdot \exp[\int_{t_1}^t dt'' \gamma(t'')]$  and where the steady-state limit of  $t_0 = -\infty$  is taken. Thus, the nonstationary flows produce a symmetric total stress tensor  $\Pi$  in a form analogous to Eq. (5.13),

$$\begin{aligned} \Pi(\mathbf{r}, t) = & p\mathbf{1} - \eta_0[\nabla\mathbf{u}(\mathbf{r}, t) + (\nabla\mathbf{u})^T] \\ & - \rho_p \int_{-\infty}^t dt' \sum_{p=1}^{n_0-1} \exp[-2(t-t')/\tau_p] \\ & \times [J_p(t-t') \cdot \nabla\mathbf{u}(\mathbf{r}', t') + (J_p \cdot \nabla\mathbf{u})^T], \end{aligned} \quad (6.3)$$

where the last term in  $(J_p \cdot \nabla\mathbf{u})^T$  is absent for elongational flows,  $\mathbf{r}' = \exp[-\int_{t_1}^t dt'' \gamma(t'')] \cdot \mathbf{r}$ , where the dynamical matrix  $J_p(t-t')$  for elongational flows has its elements given by

$$J_p(t-t') = \exp\left[\int_{t_1}^t dt'' \gamma(t'')\right] \cdot J_p \cdot \exp\left[\int_{t_1}^t dt'' \gamma^T(t'')\right], \quad (6.4a)$$

$$\begin{aligned} J_p^{ij} = & \int_{-\infty}^{t'} dt_1 \left(\frac{2}{\tau_p}\right) \exp[2(t_1 - t')/\tau_p] \\ & \times \exp\left(2 \int_{t_1}^{t'} dt_2 \dot{\gamma}_{ii}(t_2)\right) \delta_{ij}, \end{aligned} \quad (6.4b)$$

and where  $J_p$  for simple shear flows has the nonzero elements

$$\begin{aligned} J_p^{11} = & \int_{-\infty}^{t'} dt_1 \left(\frac{2}{\tau_p}\right) \exp\left(\frac{2(t-t_1)}{\tau_p}\right) \\ & \times \left[ 1 + \left( \int_{t_1}^{t'} dt_2 \dot{\gamma}_{12}(t_2) \right)^2 \right], \end{aligned} \quad (6.5a)$$

$$J_p^{22} = J_p^{33} = 1, \quad (6.5b)$$

and

$$\begin{aligned} J_p^{12} = J_p^{21} = & \int_{-\infty}^{t'} dt_1 \int_{t_1}^{t'} dt_2 \left(\frac{2}{\tau_p}\right) \\ & \times \exp(2(t_1 - t')/\tau_p) \dot{\gamma}_{12}(t_2). \end{aligned} \quad (6.5c)$$

The explicit expressions (6.3), (6.4), and (6.5) for the averaged stress tensor  $\Pi$  of the polymer solution under various types of linear flows can be used to compute several material functions that are generally considered in comparisons with experimental data. Consistent with taking the Rouse chain limit, we may approximate  $\Pi$  of Eq. (5.13) by replacing the full velocity field  $\mathbf{u}$  with the unperturbed, imposed portion  $\mathbf{v}_0$  of Eq. (2.3) because the corrections are of order  $\epsilon$  in renormalization group approaches.

Let  $\tau$  denote the nonequilibrium portion of  $\Pi$ . Straightforward algebra shows that the  $\tau$  for time-dependent linear flows has the form for shear flows

$$\begin{aligned}\tau_{ij}(t) = & -\eta_0[\dot{\gamma}_{ij}(t) + \dot{\gamma}_{ji}(t)] \\ & -\rho_p \int_{-\infty}^t dt' \sum_{p=1}^{n_0-1} \sum_{l=1}^3 \exp\left(\frac{-2(t-t')}{\tau_p}\right) \\ & \times [J_p^{il}(t-t')\dot{\gamma}_{ji}(t-t') + J_p^{jl}(t-t')\dot{\gamma}_{il}(t-t')],\end{aligned}\quad (6.6a)$$

and for elongational flows the stress tensor becomes

$$\begin{aligned}\tau_{ij}(t) = & -2\eta_0\dot{\gamma}_{ij}(t)\delta_{ij} - \rho_p \delta_{ij} \int_{-\infty}^t dt' \sum_{p=1}^{n_0-1} \\ & \times \exp[-2(t-t')/\tau_p] J_p^{ii}(t-t') \\ & \times \dot{\gamma}_{ii}(t') \exp[-\int_{t'}^t dt'' \dot{\gamma}_{ii}(t'')],\end{aligned}\quad (6.6b)$$

where the  $J_p^{ij}(t)$  for elongational and simple shear flows are presented in Eqs. (6.4) and (6.5), respectively, and the last term is omitted for the former.

Using Eq. (6.6) for the dynamical stress tensor  $\tau$ , stress growth and relaxation may readily be described. For example, suppose that the imposed flow is abruptly switched off at a time  $t^0$  before the observation time  $t$ , i.e., the time-dependent strain tensor is defined by

$$\gamma(t) = \gamma\Theta(t^0 - t). \quad (6.7)$$

It is convenient to introduce the definitions of the elongational viscosity  $\bar{\eta}^-$ , shear viscosity  $\eta^-$ , and primary normal stress coefficient  $\psi_1^-$  through

$$\begin{aligned}\tau_{11} - \tau_{33} = & -\bar{\eta}^-(t-t^0)\dot{\gamma}_{11}, \\ \tau_{12} = & -\eta^-(t-t^0)\dot{\gamma}_{12}, \\ \tau_{11} - \tau_{22} = & -\Psi_1^-(t-t^0)\dot{\gamma}_{12}^2.\end{aligned}$$

Then, the dynamical modification of the stress tensor by the polymers enables us to derive from Eqs. (6.4), (6.6), and (6.7) that

$$\begin{aligned}\bar{\eta}^-(t-t^0) = & \rho_p \sum_{p=1}^{n_0-1} (\tau_p/2)(1 - \dot{\gamma}_{11}\tau_p)^{-1} \\ & \times (1 - \dot{\gamma}_{11}\tau_p/2)^{-1} \\ & \times \exp[-2(t-t^0)/\tau_p],\end{aligned}\quad (6.8a)$$

for planar elongational flows where  $\dot{\gamma}_{11} = -\dot{\gamma}_{22}$ ,  $\dot{\gamma}_{33} = 0$ , and

$$\begin{aligned}\bar{\eta}^-(t-t^0) = & 3\rho_p \sum_{p=1}^{n_0-1} \left(\frac{\tau_p}{2}\right) [1 + (\dot{\gamma}_{11}\tau_p/2)^2] \\ & \times \{[1 - (\dot{\gamma}_{11}\tau_p/2)^2](1 - \dot{\gamma}_{11}\tau_p) \\ & \times (1 + \dot{\gamma}_{11}\tau_p/4)\}^{-1} \\ & \times \exp[-2(t-t^0)/\tau_p]\end{aligned}\quad (6.8b)$$

for three-dimensional elongations with  $\dot{\gamma}_{11} = -2\dot{\gamma}_{22} = -2\dot{\gamma}_{33}$ . Contributions from each Rouse mode decay with the corresponding Rouse relaxation times  $\tau_p/2$ . Similarly, simple shear flow is readily found to produce

$$\eta^-(t-t^0) = \rho_p \sum_{p=1}^{n_0-1} (\tau_p/2) \exp[-2(t-t^0)/\tau_p], \quad (6.9a)$$

$$\Psi_1^-(t-t^0) = 4\rho_p \sum_{p=1}^{n_0-1} (\tau_p/2)^2 \exp[-2(t-t^0)/\tau_p]. \quad (6.9b)$$

Equation (6.9a) has been previously derived from a generalized Maxwell model,<sup>4</sup> while the other results in Eqs. (6.8) and (6.9) have only been obtained for dumbbell models of polymer chains. Equations (6.8) and (6.9) exhibit several deficiencies of the simple Rouse models as these equations are independent of the rate of strain  $\dot{\gamma}$ . Corrections must arise due to fluid flow, but a treatment of this requires the introduction of hydrodynamic interactions. As is well known<sup>1,2</sup> these hydrodynamic interactions also significantly modify the polymer relaxation times  $\tau_p$  from the Rouse values. The general theory of Sec. III outlines how these hydrodynamic interactions may be incorporated into the theory, but serious technical difficulties must be overcome for their implementation.

It is likewise straightforward to describe stress under oscillatory flows for which

$$\gamma(t) = \gamma \exp(i\omega_0 t), \quad (6.10)$$

where  $\omega_0$  is the frequency of the imposed flow. For simple oscillatory shear flows the dynamical shear viscosity  $\eta(\omega_0)$  and dynamical primary normal stress coefficient  $\Psi_1(\omega_0)$  are found to be

$$\eta(\omega_0) = \eta_0 + \rho_p \sum_{p=1}^{n_0-1} \frac{(\tau_p/2)}{(1 + i\omega_0\tau_p/2)}, \quad (6.11a)$$

$$\Psi_1(\omega_0) = 4\rho_p \sum_{p=1}^{n_0-1} \frac{(\tau_p/2)^2}{(1 + i\omega_0\tau_p/2)(1 + i\omega_0\tau_p)}. \quad (6.11b)$$

Equation (6.11a) is the well-known expression for the Rouse viscosity,<sup>2</sup> and the new result in Eq. (6.11b) exhibits an interesting frequency dependence. The zero frequency limit of  $\bar{\eta}(\omega_0)$  is readily derived and is found to have a form similar to Eq. (6.8) with  $t = t^0$ . It is important to realize that Eq. (6.11a) fails to explain the important phenomenon of shear thinning, a phenomenon which likewise requires that hydrodynamic interactions be incorporated into the theory. Thus, it is expected that the relaxation times  $\tau_p$  for flowing polymers should have shear rate dependent relaxation times. In addition, we find that the Rouse model incorrectly produces a vanishing secondary normal stress coefficient.

## VII. SUMMARY

We have formulated the hydrodynamics of dilute polymer solutions under an arbitrary time-dependent linear flow within a model in which fluid convection and dynamics are ignored. The formal solutions are explicitly evaluated in the limit of a dilute solution of Rouse chains where we determine the exact dependence of the averaged solution hydrodynamics on the characteristics of the flow. This study utilizes a systematic and unified approach to treating the non-Newtonian behavior of polymer solutions. Although only the Rouse limit is explicitly considered, the general scheme outlined in Sec. III describes how hydrodynamic interactions can be included and how higher concentrations can be treated. These hydrodynamic interactions are expected to play a central role in influencing the hydrodynamics of flowing dilute polymer solutions. The present work represents the zeroth order description in a full renormalization group (RG) theory of polymer-flow systems, and we plan to develop the

RG theory by incorporating the hydrodynamic interactions in a future work.

In order to illustrate the generality of our formalism, all the material functions are systematically evaluated for various types of static and time-dependent linear flows. Several known results for shear flows are simultaneously recovered as special cases of the general theory, and other new ones are derived. Our systematic approach is a characteristic of the use of the microscopic Langevin model to derive effective hydrodynamic equations.

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## APPENDIX: EVOLUTION OF EQ. (3.13)

In order to perform the average  $\langle F_0^p \rangle$ , Eq. (3.9) for  $F_0^p$  is first integrated over the initial center-of-mass position  $\mathbf{c}_0$  [see Eq. (4.2) for the definition of  $\mathbf{c}_0$ ] to remove the delta function  $\delta(\mathbf{r} - \mathbf{c})$ . The definition (3.2) and distribution (4.5) then imply that  $\langle \mathbf{c}_0^{(0)} \rangle \equiv 0$ . It therefore follows that  $\langle F_0^p \rangle$  vanishes identically.

Notice that  $\mathbf{v}_\alpha^{(0)}$  and  $\mathbf{A}_\alpha$  in Eqs. (3.5c) and (3.6), respectively, are both of first order in the Oseen tensor  $\mathbf{T}(\mathbf{k})$  and therefore are of order  $\epsilon$  ( $\epsilon = 4 - d$ ,  $d$  is the spatial dimensionality) in a renormalization group treatment<sup>6</sup> of hydrodynamic interactions. Because we consider the Rouse limit here, we only demonstrate that the third term on the right-

hand side of Eq. (3.13) vanishes up to  $O(\epsilon)$ . Hence, to first order in  $\epsilon$ , the factor  $(1 - \mathbf{A}_\alpha)^{-1}$  can be replaced by 1. The term in question is, therefore, given to  $O(\epsilon)$  by

$$\mathbf{F}^{(0)} = n_p \langle B_\alpha \mathbf{v}_\alpha^{(0)} \rangle \equiv \mathbf{F}_1 + \mathbf{F}_2. \quad (\text{A1})$$

Insertion of Eq. (3.5c) in Eq. (A1) shows that  $\mathbf{F}_1$ , the contribution from the first term of Eq. (3.5c), is explicitly written to order  $\epsilon$  as

$$\begin{aligned} \mathbf{F}_1 = & \int_{t_0}^{\infty} dt' \int d\tau' \int d\tau'' \left\langle \delta(\mathbf{r} - \mathbf{c}) \frac{\partial^2}{\partial \tau'^2} G_0(\tau\tau'|t-t') \right. \\ & \times \mathbf{T}[\mathbf{c}_0^{(0)}(\tau', t') - \mathbf{c}_0^{(0)}(\tau'', t'')] \cdot \frac{\partial^2}{\partial \tau''^2} \mathbf{c}_0^{(0)}(\tau'', t'') \Bigg\rangle, \end{aligned} \quad (\text{A2})$$

where  $\mathbf{T}$  is the inverse Fourier transform of Eq. (3.4b). The remainder  $\mathbf{F}_2$  corresponds to the contribution from the second term of Eq. (3.5c), the one involving  $\mathbf{f}_k(t)$ , and it is defined by

$$\begin{aligned} \mathbf{F}_2 = & \int_{t_0}^{\infty} dt' \int d^d r' \int d\tau' \int d\tau'' \\ & \times \left\langle \delta(\mathbf{r} - \mathbf{c}) \frac{\partial^2}{\partial \tau'^2} G_0(\tau\tau'|t-t') \mathbf{T}(\mathbf{c}' - \mathbf{r}') \cdot \mathbf{f}(\mathbf{r}, t') \right\rangle. \end{aligned} \quad (\text{A3})$$

We evaluate  $\mathbf{F}_1$  of Eq. (A2) again by first integrating over the initial center of mass  $\mathbf{c}_0$  so that the factor of  $\delta(\mathbf{r} - \mathbf{c})$  is removed from Eq. (A2). Equation (3.3) produces the condition

$$\frac{\partial}{\partial \tau} G_0(\tau\tau'|t-t')|_{\tau=0 \text{ or } N_0} \equiv 0. \quad (\text{A4})$$

Substitution of Eq. (A4) into the average of Eq. (A2) over  $\mathbf{c}_0$  then shows  $\mathbf{F}_1$  to be identically zero.

The first order in  $\epsilon$  approximation to  $\mathbf{F}_2$  of Eq. (A3) is obtained by substitution of a first order approximation for  $\mathbf{c}'$  in the argument of  $\mathbf{T}$  in Eq. (A3) with subsequent expansion. This procedure yields

$$\begin{aligned} \mathbf{F}_2 = & \int_{t_0}^{\infty} dt' \int d\tau' \int d\tau'' \int_k \frac{\partial^2}{\partial \tau'^2} G_0(\tau\tau'|t-t') \left\langle \exp[i\mathbf{k} \cdot (\mathbf{c}^{(0)} - \mathbf{r})] \right. \\ & \times \int d^d r' \int d^d r'' \int d\tau''' \int_{t_0}^{\infty} dt'' \left\{ G_0(\tau'\tau''|t'-t'') \mathbf{T}[\mathbf{c}^{(0)}(\tau'', t'') - \mathbf{r}''] \cdot \mathbf{f}(\mathbf{r}'', t'') \cdot \frac{\partial}{\partial \mathbf{c}^{(0)}(\tau', t')} \right. \\ & \left. \left. + G_0(\tau\tau''|t-t'') i\mathbf{k} \cdot \mathbf{T}[\mathbf{c}^{(0)}(\tau'', t'') - \mathbf{r}''] \cdot \mathbf{f}(\mathbf{r}, t'') \right\} \mathbf{T}[\mathbf{c}^{(0)}(\tau', t') - \mathbf{r}'] \cdot \mathbf{f}(\mathbf{r}', t') \right\rangle, \end{aligned} \quad (\text{A5})$$

where the zeroth order contribution vanishes for the same reasons as does  $\mathbf{F}_1$ . Expressing the two  $\mathbf{T} \cdot \mathbf{f}$  factors in Eq. (A5) in terms of their Fourier transforms and averaging over  $\mathbf{f}$  with Eq. (2.2a) converts  $\mathbf{F}_2$  into

$$\begin{aligned} \mathbf{F}_2 = & \int_{t_0}^{\infty} dt' \int d\tau' \int d\tau'' \frac{\partial^2}{\partial \tau'^2} G_0(\tau\tau'|t-t') \\ & \times \int_k \langle \exp[i\mathbf{k} \cdot (\mathbf{c}^{(0)}(\tau, t) - \mathbf{r})] \mathbf{I}(\mathbf{k}, \tau' t') \rangle, \end{aligned} \quad (\text{A6})$$

where  $\mathbf{I}(\mathbf{k}, \tau' t)$  is a vector function that is independent of the initial position  $\mathbf{c}_0$  of the center of mass. Now performing the

average of Eq. (A5) over  $\mathbf{c}_0$  (a simple integration over  $\mathbf{c}_0$ ) leads to

$$\begin{aligned} \mathbf{F}_2 = & \int_{t_0}^{\infty} dt' \int d\tau' \int d\tau'' \frac{\partial^2}{\partial \tau'^2} \\ & \times G_0(\tau\tau'|t-t') \langle \mathbf{I}(\mathbf{k} = 0, \tau' t') \rangle. \end{aligned} \quad (\text{A7})$$

Use of Eq. (A4) in Eq. (A7) implies that  $\mathbf{F}_2$  vanishes identically. Thus, to order  $\epsilon$  we have

$$\mathbf{F}^{(0)} \equiv 0. \quad (\text{A8})$$

Renormalization group treatments may require a consideration of higher order terms, but these can, in principle be analyzed using the procedures outlined here.

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