Dilute Polymer Solutions in Flow: Derivation of Hydrodynamic Equations

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ABSTRACT: Starting from coupled Langevin equations for the microscopic dynamics of the polymer–solvent system, we derive the equations which govern the large-scale hydrodynamics of flowing dilute polymer solutions. More explicit results are presented for several important applied flow categories which include weak, linear, elongational, planar Couette, and Poiseuille flows.

1. Introduction

Most attempts to construct a reliable hydrodynamic description of dilute polymer solutions in flow are based on the constitutive equation approach in which the polymer contribution to the stress is evaluated by solving a diffusion-type equation for the polymer configurational distribution function in the presence of a given applied flow.[1,2] The results are then used to calculate various material functions, such as shear viscosity, stress coefficients, etc., defined as ratios of stress tensor elements to velocity gradients. Although, in principle, the strain rate in the solution can differ from that in the pure solvent (under the same externally imposed boundary conditions), giving rise to solution velocity gradient tensor type contributions to the total stress tensor, it is usually assumed that the velocity profile is not affected by the addition of a small quantity of polymer. Within this approximation the stress tensor elements that appear in the expressions for the material functions only contain the polymer contribution to the momentum transfer in the solution; flow effects enter only through the distortion of the polymer by the applied velocity gradients, and solution velocity gradient tensor type contributions are neglected.

Do polymers affect the macroscopic velocity profile in dilute solution? Even according to the constitutive equation approach, the answer to this question should be affirmative, since the polymer contribution to the stress tensor increases linearly with polymer concentration and since its substitution into the hydrodynamic equations describing the flow of the solution results in a modification of the applied velocity field (and, hence, of the velocity gradients) that is likewise proportional to the polymer concentration. Consequently, the neglect of the polymer-induced modification of the solvent velocity gradient tensor cannot be justified in general,[3] and effects of this type should be observable in local measurements of solution velocity profiles.

Recently several attempts have been made by the present authors to deal with flow modification in dilute polymer solutions,[4–7] all of them based on the coupled stochastic differential (Langevin) equations approach to the microscopic dynamics of the polymer–solvent system.[8] The case of weak but otherwise arbitrary applied flow is considered in ref 4 where an effective hydrodynamic equation for the solution is derived, which turns out to be identical with the generalized Maxwell model known from the theory of viscoelastic fluids.[9] References 5 and 6 derive the general theory for the case of arbitrarily strong linear applied flows; explicit expressions for the polymer contribution to the stress tensor are given for simple shear and elongational flows as a function of the applied velocity gradients. A brief account of the present derivation of the effective macroscopic equations, which govern the hydrodynamics of dilute polymer solutions subjected (through the boundary conditions) to arbitrary applied flow, has been given in ref 7.

Section 2 presents a detailed derivation of the linear integrodifferential hydrodynamic equations for dilute polymer solutions subjected to general applied flows. More explicit results are derived in section 3 for several important applied flow categories which include weak, general linear, elongational, planar Couette, and Poiseuille flows, and whenever possible, the results are compared with previous work. In section 4 we discuss the main assumptions and approximations behind our model and outline directions for future theoretical and experimental research.

2. The Model

We start with the coupled stochastic differential equations describing the polymer and solvent dynamics[8]

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

$$\partial \mathbf{u}(\mathbf{x},t)/\partial t = \eta_0 \Delta \mathbf{u}(\mathbf{x},t) - \mathbf{u}(\mathbf{x},t)\cdot\nabla \mathbf{u}(\mathbf{x},t) - \nabla P(\mathbf{x},t) + \mathbf{F}(\mathbf{x},t) + \mathbf{f}(\mathbf{x},t) \quad (2.2)$$

$$\nabla\cdot\mathbf{u}(\mathbf{x},t) = 0 \quad (2.3)$$

where θ and $\mathbf{f}$ are Gaussian noises with zero mean and correlators

$$\langle \theta_\alpha(\tau,t)\theta_\beta(\tau',t')\rangle = 2\xi_0^{-1}\delta_{\alpha\beta}\delta(\tau-\tau')\delta(t-t')\mathbf{1} \quad (2.4)$$

and

$$\langle \mathbf{f}(\mathbf{x},t)\mathbf{f}(\mathbf{x}',t')\rangle = -2\eta_0\Delta\delta(\mathbf{x}-\mathbf{x}')\delta(t-t')\mathbf{1} \quad (2.5)$$

Here, $\mathbf{u}(\mathbf{x},t)$ and $P(\mathbf{x},t)$ are, respectively, the velocity and pressure fields at position $\mathbf{x}$ and time t, $\mathbf{c}_\alpha(\tau,t)$ is the position of the τth monomer on the αth polymer, ξ_0 is the (bare) monomer friction coefficient, η_0 is the solvent viscosity (using units in which the solvent density is unity), and $\mathbf{1}$ is the unit tensor. Excluded-volume effects are ignored but can, however, be readily introduced into the

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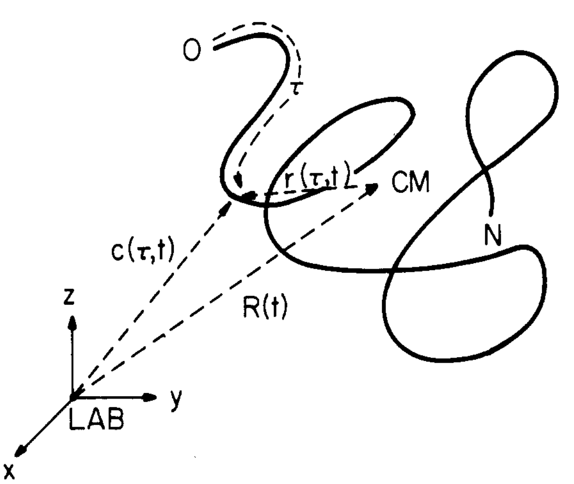

Figure 1. Position vector of the τth monomer on the polymer in laboratory fixed ($\mathbf{c}(\tau,t)$) and center of mass ($\mathbf{r}(\tau,t)$) coordinates.

model. The polymer force on the solvent, $\mathbf{F}(\mathbf{x},t)$, follows from eq 2.1 and Newton's 3rd law[10] as

$$\mathbf{F}(\mathbf{x},t) = \sum_{\alpha} \int_0^N \mathrm{d}\tau \, \frac{\partial^2 \mathbf{c}_\alpha(\tau,t)}{\partial \tau^2} \, \delta(\mathbf{x}-\mathbf{c}_\alpha(\tau,t)) \qquad (2.6)$$

where N is the "number" of monomers and $\alpha = 1, 2, ..., n_\mathrm{p}$, with n_p being the number of polymers in the solution volume V, and the continuous chain limit is taken. In order to simplify the notation, the index α on the polymer position vectors is suppressed in the following; this introduces no ambiguity provided that hydrodynamic interference between different polymers is neglected, an approximation that becomes exact in the dilute solution limit. In the absence of polymers, eq 2.2 reduces to model A of fluctuating hydrodynamics,[11,12] which is discussed in great detail in ref 11. Furthermore, the noise term in eq 2.2 plays an important role in the context of polymer solutions and, as has been shown by one of the present authors,[13] it is precisely the hydrodynamic noise term that is responsible for the appearance of hydrodynamic interaction tensors in the diffusion equation for the polymer distribution function.[1,2]

The center of mass (CM) position of a polymer is defined by

$$\mathbf{R}(t) = N^{-1} \int_0^N \mathrm{d}\tau \, \mathbf{c}(\tau,t) \qquad (2.7)$$

and the location of a monomer at the contour point τ with respect to the CM is (Figure 1)

$$\mathbf{r}(\tau,t) = \mathbf{c}(\tau,t) - \mathbf{R}(t) \qquad (2.8)$$

Notice that the magnitude of the relative coordinate $\mathbf{r}(\tau,t)$ is, at most, of the order of polymer dimensions. Since we are interested in the influence of a polymer on fluid motions on scales much larger than the polymer size, the velocity field is expanded about the CM and only terms linear in $\mathbf{r}$, are kept

$$\mathbf{u}[\mathbf{c}(\tau,t),t] = \mathbf{u}[\mathbf{R}(t),t] + \mathbf{r}(\tau,t)\cdot\nabla\mathbf{u}[\mathbf{R}(t),t] \qquad (2.9)$$

In view of its importance for our considerations we stress that this assumption of a small variation of the solvent velocity field on the polymer scale is an excellent approximation for experimentally realizable *macroscopic* flows. The approximation holds even for rapidly varying flows in which the flow time scale is shorter than the polymer relaxation time (Deborah number > 1). Although this assumption is by no means obvious for the microscopic fluctuating solvent velocity field, in this work we only deal with the effect of polymers on the macroscopic hydrodynamics of the fluid and either neglect the microscopic velocity field (Rouse-type approximation) or assume that it serves to renormalize the polymer relaxation spectrum such that all the Rouse relaxation rates are replaced by their appropriate non-free-draining counterparts.

With differentiation of eq 2.7 with respect to time and use of eq 2.1, 2.8, and 2.9, eq 2.1 is transformed to

$$\partial\mathbf{R}(t)/\partial t = \mathbf{u}[\mathbf{R}(t),t] + N^{-1} \int_0^N \mathrm{d}\tau' \, \theta(\tau',t) \qquad (2.10)$$

and

$$\frac{\partial \mathbf{r}(\tau,t)}{\partial t} = \xi_0^{-1} \frac{\partial^2 \mathbf{r}(\tau,t)}{\partial \tau^2} + \mathbf{r}(\tau,t)\cdot\nabla\mathbf{u}[\mathbf{R}(t),t] + \theta(\tau,t) - N^{-1} \int_0^N \mathrm{d}\tau' \, \theta(\tau',t) \qquad (2.11)$$

In order to simplify the analysis, we neglect the diffusion of CM by dropping the $\int \mathrm{d}\tau' \, \theta(\tau',t)$ term in eq 2.10 and 2.11. This introduces a negligible error in the consideration of polymer motion along flow streamlines but may result in considerable deviations from the correct description of the long-time motion across these streamlines. However, here we only study the effect of polymers on the large-scale dynamics of the fluid, and it can be shown that polymer diffusion contributes a factor of $D_\mathrm{p}k^2$ to the hydrodynamic relaxation on scale k^{-1} (D_p is the polymer diffusion coefficient and k is the wavevector of the hydrodynamic mode). Since $D_\mathrm{p}/\eta_0 < 10^{-5}$ for typical polymer–solvent combinations, $D_\mathrm{p}k^2$ is negligible compared to the viscous dissipation rate $\eta_0 k^2$. If order $1/N$ corrections in eq 2.11 are neglected, eq 2.10 and 2.11 are replaced in this approximation by

$$\partial\mathbf{R}(t)/\partial t = \mathbf{u}[\mathbf{R}(t),t] \qquad (2.12)$$

and

$$\frac{\partial \mathbf{r}(\tau,t)}{\partial t} = \xi_0^{-1} \frac{\partial^2 \mathbf{r}(\tau,t)}{\partial \tau^2} + \mathbf{r}(\tau,t)\cdot\nabla\mathbf{u}[\mathbf{R}(t),t] + \theta(\tau,t) \qquad (2.13)$$

Now decompose the macroscopic velocity field in the form

$$\mathbf{u}(\mathbf{x},t) = \mathbf{v}_0(\mathbf{x},t) + \mathbf{v}(\mathbf{x},t) \qquad (2.14)$$

such that $\mathbf{v}_0(\mathbf{x},t)$ is an arbitrary externally applied velocity field (the solution of eq 2.2 and 2.3 in the absence of polymers and neglecting the solvent fluctuations) and $\mathbf{v}(\mathbf{x},t)$ is the deviation from this velocity profile due to the influence of polymers on the solvent or due to other, unspecified, hydrodynamic disturbances. A similar decomposition follows for the pressure field

$$P(\mathbf{x},t) = p_0(\mathbf{x},t) + p(\mathbf{x},t) \qquad (2.15)$$

We assume that $\mathbf{v}$ is small and linearize the Navier–Stokes equation about the applied flow. Neglecting the terms that are nonlinear in $\mathbf{v}$ in eq 2.2, converts (2.2) into

$$\partial\mathbf{v}(\mathbf{x},t)/\partial t = \eta_0\Delta\mathbf{v}(\mathbf{x},t) - \mathbf{v}_0(\mathbf{x},t)\cdot\nabla\mathbf{v}(\mathbf{x},t) - \mathbf{v}(\mathbf{x},t)\cdot\nabla\mathbf{v}_0(\mathbf{x},t) - \nabla p(\mathbf{x},t) + \mathbf{F}(\mathbf{x},t) \qquad (2.16)$$

and

$$\nabla\cdot\mathbf{v}(\mathbf{x},t) = 0 \qquad (2.17)$$

where the fluctuating force $\mathbf{f}$ has been dropped (hydrodynamic fluctuations are expected to be unimportant for the large-scale dynamics of the solvent).

Inspection of eq 2.6, 2.12, and 2.13 leads to the conclusion that the polymer force on the fluid $\mathbf{F}(\mathbf{x},t)$ is a functional of the velocity field $\mathbf{u}(\mathbf{x},t)$, and a self-consistent application of the linearization approximation (in $\mathbf{v}$) implies that $\mathbf{F}(\mathbf{x},t)$ should be evaluated to first order in $\mathbf{v}(\mathbf{x},t)$.

This, in turn, means that $\mathbf{R}(t)$ and $\mathbf{r}(t)$ should be evaluated to first order in v in eq 2.12 and 2.13. Denoting

$$\mathbf{R}(t) = \mathbf{R}_0(t) + \mathbf{R}_1(t) \tag{2.18}$$

and

$$\mathbf{r}(\tau,t) = \mathbf{r}_0(\tau,t) + \mathbf{r}_1(\tau,t) \tag{2.19}$$

with $\mathbf{R}_i$ and $\mathbf{r}_i$ of ith order in v, eq 2.12 becomes

$$\partial \mathbf{R}_0(t)/\partial t = \mathbf{v}_0[\mathbf{R}_0(t),t] \tag{2.20}$$

$$\partial \mathbf{R}_1(t)/\partial t = \mathbf{\Gamma}_0[\mathbf{R}_0(t),t]\cdot\mathbf{R}_1(t) + \mathbf{v}[\mathbf{R}_0(t),t] \tag{2.21}$$

with

$$\mathbf{\Gamma}_0(\mathbf{R}_0(t),t) = \{\nabla \mathbf{v}_0[\mathbf{R}_0(t),t]\}^{\mathrm{T}} \tag{2.22}$$

where $\mathbf{A}^{\mathrm{T}}$ is the transpose of the tensor $\mathbf{A}$.

The applied flow $\mathbf{v}_0$ is assumed to be "switched on" at time $t = 0$. For a given $\mathbf{v}_0$ we can solve eq 2.20 and obtain $\mathbf{R}_0(t) = \mathbf{R}_0[\mathbf{R}(0),t]$ as a function of the initial CM position $\mathbf{R}(0)$ and of the time t. Substituing $\mathbf{R}_0(t)$ into eq 2.21 and using the initial condition $\mathbf{R}_1(0) = 0$ give

$$\mathbf{R}_1(t) = \mathbf{g}(t)\cdot\int_0^t \mathrm{d}t'\, \mathbf{g}^{-1}(t')\cdot\mathbf{v}[\mathbf{R}_0(t'),t'] \tag{2.23}$$

where $\mathbf{g}(t)$ is formally represented as a time-ordered exponential ($\mathbf{T}$ is the time-ordering operator)

$$\mathbf{g}[\mathbf{R}(0),t] = \mathbf{T}e^{\int_0^t \mathrm{d}t' \mathbf{\Gamma}_0[\mathbf{R}_0(t'),t']} \equiv 1 + \int_0^t \mathrm{d}t'\, \mathbf{\Gamma}_0(t') + \int_0^t \mathrm{d}t' \int_0^{t'} \mathrm{d}t''\, \mathbf{\Gamma}_0(t')\cdot\mathbf{\Gamma}_0(t'') + \int_0^t \mathrm{d}t' \int_0^{t'} \mathrm{d}t'' \int_0^{t''} \mathrm{d}t'''\, \mathbf{\Gamma}_0(t')\cdot\mathbf{\Gamma}_0(t'')\cdot\mathbf{\Gamma}_0(t''') + \ldots \tag{2.24}$$

and $\mathbf{g}^{-1}$ is its inverse. Notice that $\mathbf{\Gamma}_0[\mathbf{R}_0(t'),t']$ is a function of the Lagrangian coordinate $\mathbf{R}_0(t')$, i.e., of the position at time t' of the center of mass of a polymer that is freely advected by the applied velocity field $\mathbf{v}_0$, given that it will be at position $\mathbf{R}_0(t)$ at time t (or, equivalently, that it was at $\mathbf{R}(0)$ at $t = 0$). Consequently, $\mathbf{g}(t)$ is a function of $\mathbf{R}_0(t)$ (or of $\mathbf{R}(0)$). It is important to notice that while $\mathbf{g}(t)$ can be evaluated explicitly (see section 3) for several important categories of applied flows (for example, linear flows or flows with time-independent velocity gradients such as Poiseuille flow), only approximate results can be obtained for more complicated flow profiles for which the series expansion of the time-ordered exponent in (2.24) cannot be resummed analytically. In the rheological literature, $\mathbf{g}$ is better known as the displacement gradient tensor and is usually evaluated from the defining differential equation (p 431 in ref 14) rather than using the explicit solution, eq 2.24.

Separating the contributions of the zeroth- and first-order terms (in v) in eq 2.13 yields

$$\frac{\partial \mathbf{r}_0(\tau,t)}{\partial t} = \xi_0^{-1}\frac{\partial^2 \mathbf{r}_0(\tau,t)}{\partial \tau^2} + \mathbf{\Gamma}_0[\mathbf{R}_0(t),t]\cdot\mathbf{r}_0(\tau,t) + \boldsymbol{\theta}(\tau,t) \tag{2.25}$$

$$\frac{\partial \mathbf{r}_1(\tau,t)}{\partial t} = \xi_0^{-1}\frac{\partial^2 \mathbf{r}_1(\tau,t)}{\partial \tau^2} + \mathbf{\Gamma}_0[\mathbf{R}_0(t),t]\cdot\mathbf{r}_1(\tau,t) + \mathbf{\Gamma}_1[\mathbf{R}_0(t),t]\cdot\mathbf{r}_0(\tau,t) + \left\{\mathbf{R}_1(t)\cdot\frac{\partial}{\partial \mathbf{R}_0(t)}\mathbf{\Gamma}_0[\mathbf{R}_0(t),t]\right\}\cdot\mathbf{r}_0(\tau,t) \tag{2.26}$$

where

$$\mathbf{\Gamma}_1[\mathbf{R}_0(t),t] = \{\nabla \mathbf{v}[\mathbf{R}_0(t),t]\}^{\mathrm{T}} \tag{2.27}$$

Integrating eq 2.25 we obtain

$$\mathbf{r}_0(\tau,t) = \mathbf{g}(t)\cdot\int_0^N \mathrm{d}\tau'\, G_0(\tau,\tau'|t)\mathbf{r}(\tau') + \int_0^t \mathrm{d}t' \int_0^N \mathrm{d}\tau'\, G_0(\tau,\tau'|t-t')\mathbf{g}(t)\cdot\mathbf{g}^{-1}(t')\cdot\boldsymbol{\theta}(\tau',t') \tag{2.28}$$

where $\mathbf{r}(\tau')$ is the initial position of the τth segment and where the zero-flow (Rouse chain) Green function G_0 is given by

$$G_0(\tau,\tau'|t-t') = 2N^{-1}\Theta(t-t')\sum_{p=1}^{\infty} \cos \hat{p}\tau \cos \hat{p}\tau' e^{-\lambda_p(t-t')} \tag{2.29}$$

with

$$\hat{p} \equiv \pi p/N \tag{2.30}$$

$$\lambda_p = \hat{p}^2/\xi_0 \tag{2.31}$$

Here, λ_p is the relaxation rate of the pth Rouse mode and Θ is the step function (the definition of the Green function omits the constant $p = 0$ term that corresponds to the translation of the CM). Solving eq 2.26 with the initial condition $\mathbf{r}_1(0) = 0$ produces

$$\mathbf{r}_1(\tau,t) = \mathbf{g}(t)\cdot\int_0^t \mathrm{d}t' \int_0^N \mathrm{d}\tau'\, G_0(\tau,\tau'|t-t')\mathbf{g}^{-1}(t')\cdot\left\{\mathbf{\Gamma}_1[\mathbf{R}_0(t'),t'] + \mathbf{R}_1(t')\cdot\frac{\partial}{\partial \mathbf{R}_0(t')}\,\mathbf{\Gamma}_0[\mathbf{R}_0(t'),t']\right\}\cdot\mathbf{r}_0(\tau',t') \tag{2.32}$$

We now return to eq 2.16 and average it with respect to the polymer degrees of freedom at the initial time $t = 0$. In particular, it is necessary to evaluate the average of the polymer force on the fluid $\mathbf{F}(\mathbf{x},t)$, defined in eq 2.6. First, average with respect to the initial position of the CM; i.e., integrate over all $\mathbf{R}(0)$ within volume V and divide by the volume. Since different polymers are assumed to contribute incoherently, the summation over the polymer index produces a factor of n_{p} (number of polymers in volume V). Denoting the CM average by $\langle\ \rangle_{\mathrm{R}}$, this average of (2.6) is written using (2.8) as

$$\begin{aligned}\langle \mathbf{F}(\mathbf{x},t)\rangle_{\mathrm{R}} &= \rho\int_V \mathrm{d}\mathbf{R}(0) \int_0^N \mathrm{d}\tau\, \frac{\partial^2 \mathbf{r}(\tau,t)}{\partial \tau^2}\delta[\mathbf{x}-\mathbf{R}(t)-\mathbf{r}(\tau,t)] \\ &= \rho\int_V \mathrm{d}\mathbf{R}(0) \int_0^N \mathrm{d}\tau\, \frac{\partial^2 \mathbf{r}(\tau,t)}{\partial \tau^2}e^{-\mathbf{r}(\tau,t)\cdot\partial/\partial\mathbf{x}}\delta[\mathbf{x}-\mathbf{R}_0(t)-\mathbf{R}_1(t)]\end{aligned} \tag{2.33}$$

where we introduce the polymer number concentration $\rho = n_{\mathrm{p}}/V$ and formally expand the δ-function about the CM position through a Taylor expansion of the exponential in the second line of (2.33). Such an expansion is convenient since we are only interested in hydrodynamic scales that are much larger than the polymer size and thus only the first few terms in the expansion need be considered. Expanding the exponent it is found that the zeroth-order term vanishes upon τ integration. The first-order term (in $\mathbf{r}\cdot\partial/\partial\mathbf{x}$) gives

$$\langle \mathbf{F}(\mathbf{x},t)\rangle_{\mathrm{R}} = -\rho\int_V \mathrm{d}\mathbf{R}(0) \int_0^N \mathrm{d}\tau\, \frac{\partial^2 \mathbf{r}(\tau,t)}{\partial \tau^2}\mathbf{r}(\tau,t)\cdot\frac{\partial}{\partial \mathbf{x}}\delta[\mathbf{x}-\mathbf{R}_0(t)-\mathbf{R}_1(t)] \tag{2.34}$$

Since nonlinear terms in v are neglected and since $\mathbf{R}_1$ is a linear functional of v, we expand the δ-function to first order in $\mathbf{R}_1$ and average over the polymer degrees of freedom

$$\langle\langle \mathbf{F}(\mathbf{x},t)\rangle\rangle = -\rho\int_V \mathrm{d}\mathbf{R}(0)\int_0^N \mathrm{d}\tau \left\{\left\langle \frac{\partial^2\mathbf{r}_1(\tau,t)}{\partial\tau^2}\mathbf{r}_0(\tau,t)\right\rangle + \left\langle \frac{\partial^2\mathbf{r}_0(\tau,t)}{\partial\tau^2}\mathbf{r}_1(\tau,t)\right\rangle + \left\langle \frac{\partial^2\mathbf{r}_0(\tau,t)}{\partial\tau^2}\mathbf{r}_0(\tau,t)\cdot\left[1-\frac{\partial}{\partial\mathbf{x}}\mathbf{R}_1(t)\right]\right\rangle\right\}\cdot\frac{\partial}{\partial\mathbf{x}}\delta[\mathbf{x}-\mathbf{R}_0(t)] \quad (2.35)$$

where $\langle\ \rangle$ denotes the average over both the initial relative coordinate $\mathbf{r}(\tau)$ and random noise $\theta(\tau,t)$ and where $\langle\langle\ \rangle\rangle \equiv \langle\langle\ \rangle_{\mathrm{R}}\rangle$.

A similar averaging procedure can be formally applied to the linearized Navier-Stokes equation (eq 2.16, 2.17) producing the following hydrodynamic equations for dilute polymer solutions in flow:

$$\partial\langle\langle \mathbf{v}(\mathbf{x},t)\rangle\rangle/\partial t = \eta_0\Delta\langle\langle \mathbf{v}(\mathbf{x},t)\rangle\rangle - \mathbf{v}_0(\mathbf{x},t)\cdot\nabla\langle\langle \mathbf{v}(\mathbf{x},t)\rangle\rangle - \langle\langle \mathbf{v}(\mathbf{x},t)\rangle\rangle\cdot\nabla\mathbf{v}_0(\mathbf{x},t) - \nabla\langle\langle p(\mathbf{x},t)\rangle\rangle + \langle\langle \mathbf{F}(\mathbf{x},t)\rangle\rangle \quad (2.36)$$

$$\nabla\cdot\langle\langle \mathbf{v}(\mathbf{x},t)\rangle\rangle = 0 \quad (2.37)$$

Our next goal is to obtain a system of closed linear equations for the velocity field $\langle\langle \mathbf{v}\rangle\rangle$ by deriving explicit expressions for the average force $\langle\langle \mathbf{F}\rangle\rangle$ exerted by the polymers on the solvent, in terms of polymer parameters, applied flow, and the unknown velocity field $\langle\langle \mathbf{v}\rangle\rangle$. The difficulty is that both $\mathbf{R}_1$ and $\mathbf{r}_1$ are linear functionals of $\mathbf{v}$ (eq 2.23 and 2.32), and since $\mathbf{v}(\mathbf{x},t) = \mathbf{v}(\mathbf{x},t|\{\mathbf{R}_0,\mathbf{r}_0\})$ is a functional of the polymer coordinates (through eq 2.16), the expression for the polymer force on the fluid contains terms of the type $\langle\langle \mathbf{r}_0\mathbf{r}_0\mathbf{v}\rangle\rangle$ and $\langle\langle \mathbf{r}_0\mathbf{r}_0\boldsymbol{\Gamma}_1\rangle\rangle$, in which the polymer and flow variables are correlated. In order to obtain a closed equation for $\langle\langle \mathbf{v}\rangle\rangle$, we introduce a decoupling approximation of the kind made in mode-coupling theories[15]

$$\langle\langle \mathbf{r}_0\mathbf{r}_0\mathbf{v}\rangle\rangle \to \langle\langle \mathbf{r}_0\mathbf{r}_0\rangle\rangle\langle\langle \mathbf{v}\rangle\rangle;\qquad \langle\langle \mathbf{r}_0\mathbf{r}_0\boldsymbol{\Gamma}_1\rangle\rangle \to \langle\langle \mathbf{r}_0\mathbf{r}_0\rangle\rangle\langle\langle \boldsymbol{\Gamma}_1\rangle\rangle \quad (2.38)$$

and in the following we replace $\mathbf{v}$ by $\langle\langle \mathbf{v}\rangle\rangle$ in the definitions of $\mathbf{R}_1$ and $\mathbf{r}_1$ (eq 2.23 and 2.32). Notice that since the above averages occur in the polymer force term $\langle\langle \mathbf{F}\rangle\rangle$, which is proportional to the coupling between the polymer and solvent, and since deviations from the decoupling approximation arise due to the dependence of $\mathbf{v}$ on $\mathbf{r}_0$, the deviations are of second order in the polymer–solvent coupling. Although no systematic treatment of this coupling is attempted here, it is known to be small in the sense of renormalization group treatments.[16]

Returning to eq 2.35, use is made of the fact that due to incompressibility and mass conservation, the Jacobian of the transformation $\mathbf{R}(0) \to \mathbf{R}_0(t)$ is unity.[14] Changing variables and performing the $\mathbf{R}_0(t)$ integration give

$$\langle\langle F_i(\mathbf{x},t)\rangle\rangle = -\rho\sum_{j=1}^{3}\frac{\partial}{\partial x_j}\int_0^N \mathrm{d}\tau\left\{\left[1-\sum_{k=1}^{3}\frac{\partial}{\partial x_k}\langle\langle R_{1k}(t)\rangle\rangle\right]\times\left\langle \frac{\partial^2 r_{0i}(\tau,t)}{\partial\tau^2}r_{0j}(\tau,t)\right\rangle + \left\langle \frac{\partial^2 r_{0i}(\tau,t)}{\partial\tau^2}r_{1j}(\tau,t)\right\rangle + \left\langle \frac{\partial^2 r_{1i}(\tau,t)}{\partial\tau^2}r_{0j}(\tau,t)\right\rangle\right\} \quad (2.39)$$

where $\partial/\partial x_k$ operates on the product $\langle\langle R_{1k}\rangle\rangle\langle(\partial^2 r_{0i}/\partial\tau^2)r_{0j}\rangle$ and $\partial/\partial x_j$ operates on the whole integrand ($\mathbf{R}_1$, $\mathbf{r}_1$, and $\mathbf{r}_0$ are functions of $\mathbf{x}$, through the $\mathbf{x}$ dependence of $\boldsymbol{\Gamma}_0$, $\mathbf{v}$, and $\boldsymbol{\Gamma}_1$).

With the definition of the average polymer force on the fluid as a divergence of a symmetric stress tensor σ given by

$$\langle\langle \mathbf{F}(\mathbf{x},t)\rangle\rangle = -\nabla\cdot\sigma(\mathbf{x},t) \quad (2.40)$$

comparison of eq 2.39 and 2.40 yields

$$\sigma(\mathbf{x},t) = \rho\int_0^N \mathrm{d}\tau\left\{\left[1-\frac{\partial}{\partial\mathbf{x}}\cdot\langle\langle \mathbf{R}_1(t)\rangle\rangle\right]\times\left\langle \frac{\partial^2\mathbf{r}_0(\tau,t)}{\partial\tau^2}\mathbf{r}_0(\tau,t)\right\rangle + \left\langle \frac{\partial^2\mathbf{r}_1(\tau,t)}{\partial\tau^2}\mathbf{r}_0(\tau,t)\right\rangle + \left\langle \frac{\partial^2\mathbf{r}_0(\tau,t)}{\partial\tau^2}\mathbf{r}_1(\tau,t)\right\rangle\right\}^{\mathrm{T}} \quad (2.41)$$

where $\mathbf{r}_1$ is a linear functional of $\langle\langle \boldsymbol{\Gamma}_1\rangle\rangle$ and $\langle\langle \mathbf{v}\rangle\rangle$. Neglecting the terms containing $\mathbf{v}$ (e.g., $\mathbf{R}_1$ and $\mathbf{r}_1$) in eq 2.41, one recovers the stress–strain rate relation familiar from the kinetic theory of polymeric liquids (compare with eq 10.4–6 in ref 1, for the linear dumbbell case). The terms containing $\mathbf{v}$ express the deviation of the solution velocity field from an assumed homogeneous flow profile. Notice that it is only the divergence of the stress tensor that is derived directly from the Langevin equations (eq 2.1–2.3) and that the stress tensor itself is not uniquely defined by this procedure. In fact, we can add to it any tensor σ' that satisfies $\nabla\cdot\sigma' = 0$, without affecting the hydrodynamics of the fluid (eq 2.36). We, however, use the above definition of the stress tensor (eq 2.41) in the following.

Introducing the expressions for the various averages in eq 2.41, derived in the Appendix, provides the stress tensor for dilute polymer solutions in general applied flow[7] as

$$\sigma(\mathbf{x},t) = -\rho\sum_{p=1}^{\infty}e^{-2\lambda_p t}\cdot\left\{\beta(t)[\mathbf{g}(t)\cdot\boldsymbol{\Lambda}(p,t)\cdot\mathbf{g}^{\mathrm{T}}(t)] + \int_0^t \mathrm{d}t'\,\mathbf{g}(t)\cdot[\mu(t')\cdot\boldsymbol{\Lambda}(p,t') + \boldsymbol{\Lambda}(p,t')\cdot\mu^{\mathrm{T}}(t')]\cdot\mathbf{g}^{\mathrm{T}}(t)\right\} \quad (2.42)$$

where we define the scalar operator β (the divergence operates on everything on its right)

$$\beta(t) = 1 - \frac{\partial}{\partial\mathbf{x}}\cdot\int_0^t \mathrm{d}t'\,\mathbf{g}(t)\cdot\mathbf{g}^{-1}(t')\cdot\langle\langle \mathbf{v}[\mathbf{x}'(t'),t']\rangle\rangle \quad (2.43)$$

the tensor

$$\mu(t') = \mathbf{g}^{-1}(t')\cdot\langle\langle \boldsymbol{\Gamma}_1[\mathbf{x}'(t'),t']\rangle\rangle\cdot\mathbf{g}(t') + \int_0^{t'}\mathrm{d}t''\,\{\mathbf{g}^{-1}(t'')\cdot\langle\langle \mathbf{v}[\mathbf{x}''(t''),t'']\rangle\rangle\}\cdot\left\{\frac{\partial}{\partial\mathbf{x}'}\boldsymbol{\Gamma}_0[\mathbf{x}'(t'),t']\right\}\cdot\mathbf{g}(t') \quad (2.44)$$

and the symmetric tensor

$$\boldsymbol{\Lambda}(p,t) = 1 + 2\lambda_p\int_0^t \mathrm{d}t'\,e^{2\lambda_p t'}[\mathbf{g}^{\mathrm{T}}(t')\cdot\mathbf{g}(t')]^{-1} \quad (2.45)$$

The above scalar and tensors are functions of $\mathbf{x}$; $\beta(t)$ and $\mu(t)$ are linear functionals of $\langle\langle \mathbf{v}\rangle\rangle$ and $\langle\langle \boldsymbol{\Gamma}_1\rangle\rangle$. Notice that the argument $\mathbf{x}'$ of $\langle\langle \mathbf{v}\rangle\rangle$ and $\langle\langle \boldsymbol{\Gamma}_1\rangle\rangle$ is to be interpreted as a Lagrangian coordinate, i.e., as the position at time t' of a fluid element moving with the velocity $\mathbf{v}_0$ given that at time t it will be at position $\mathbf{x}$. Thus

$$\langle\langle \mathbf{v}[\mathbf{x}'(t'),t']\rangle\rangle \equiv \int_V \mathrm{d}\mathbf{R}_0\,(0)\delta[\mathbf{x}-\mathbf{R}_0(t)]\langle \mathbf{v}[\mathbf{R}_0(t'),t']\rangle \quad (2.46)$$

$\langle\langle \boldsymbol{\Gamma}_1[\mathbf{x}'(t'),t']\rangle\rangle$ is similarly defined. Although, strictly speaking, the Rouse model relaxation rates λ_p of eq 2.31 should be used, we may adopt a "preaveraging" approximation of the kind discussed in ref 4 and introduce hydrodynamically "dressed" relaxation rates.

Equations 2.36, 2.37, 2.40, and 2.42 form the basis of macroscopic hydrodynamics of dilute polymer solutions and the following section derives more explicit hydrodynamic equations for several important cases.

3. Special Cases

1. **"Weak" Flow.** In the limit of constant (in space) applied flow eq 2.22 implies

$$\mathbf{\Gamma}_0 = 0 \qquad (3.1)$$

and then it follows that

$$\mathbf{g} = 1 \qquad (3.2)$$

$$\mathbf{x}'(t') = \mathbf{x} \qquad (3.3)$$

$$\mathbf{\Lambda}(p,t) = e^{2\lambda_p t}\mathbf{1} \qquad (3.4)$$

and

$$\beta = 1 \qquad (3.5)$$

Evaluating (2.42) gives

$$\langle\langle \mathbf{F}(\mathbf{x},t)\rangle\rangle = \rho \sum_{p=1}^{\infty} \int_0^t \mathrm{d}t'\, e^{-2\lambda_p(t-t')} \Delta \langle\langle \mathbf{v}(\mathbf{x},t')\rangle\rangle \qquad (3.6)$$

identical with the weak flow result derived by one of us[4] (also known as the generalized Maxwell model[9]).

2. **Steady Linear Flow.** Here the flow is specified by

$$\mathbf{v}_0(\mathbf{x}) = \mathbf{\Gamma}_0\cdot\mathbf{x} \qquad (3.7)$$

and we compute

$$\mathbf{g}(t) = e^{\mathbf{\Gamma}_0 t} \qquad (3.8)$$

$$\mathbf{x}'(t') = e^{-\mathbf{\Gamma}_0(t-t')}\cdot\mathbf{x} \qquad (3.9)$$

and

$$\beta = 1 \qquad (3.10)$$

By substitution of (3.7)–(3.10) into (2.40) and (2.42) and use of the incompressibility condition, (2.37) produces

$$\langle\langle \mathbf{F}(\mathbf{x},t)\rangle\rangle = \rho \sum_{p=1}^{\infty} e^{-2\lambda_p t} \frac{\partial}{\partial \mathbf{x}}\cdot\left[e^{\mathbf{\Gamma}_0 t}\cdot \int_0^t \mathrm{d}t'\, \mathbf{\Lambda}(p,t')\cdot\boldsymbol{\mu}^{\mathrm{T}}(t')\cdot e^{\mathbf{\Gamma}_0^{\mathrm{T}} t}\right] \qquad (3.11)$$

where

$$\mathbf{\Lambda}(p,t') = \mathbf{1} + 2\lambda_p \int_0^{t'} \mathrm{d}t''\, e^{2\lambda_p t''} e^{-\mathbf{\Gamma}_0 t''}\cdot e^{-\mathbf{\Gamma}_0^{\mathrm{T}} t''} \qquad (3.12)$$

and

$$\boldsymbol{\mu}^{\mathrm{T}}(t') = e^{\mathbf{\Gamma}_0^{\mathrm{T}} t'}\cdot\frac{\partial}{\partial \mathbf{x}'}\langle\langle \mathbf{v}(\mathbf{x}',t')\rangle\rangle\cdot e^{-\mathbf{\Gamma}_0^{\mathrm{T}} t'} \qquad (3.13)$$

a. Elongational Flow. For this class of potential (vorticity free) flows, the velocity gradient matrix is diagonal

$$\mathbf{\Gamma}_0 = \begin{pmatrix} \gamma_1 & 0 & 0 \\ 0 & \gamma_2 & 0 \\ 0 & 0 & \gamma_3 \end{pmatrix} \qquad (3.14)$$

and substitution into eq 3.8 and 3.9 gives (no summation over repeated indices)

$$[\mathbf{g}(t)]_{ij} = \delta_{ij} e^{\gamma_i t} \qquad (3.15)$$

$$x'_i(t') = e^{-\gamma_i(t-t')} x_i \qquad (3.16)$$

and

$$\frac{\partial}{\partial x'_i} = e^{\gamma_i(t-t')}\frac{\partial}{\partial x_i} \qquad (3.17)$$

After some simple algebra we find (from eq 3.11)

$$\langle\langle F_i(\mathbf{x},t)\rangle\rangle = \rho \sum_{p=1}^{\infty} \sum_{j=1}^{3} (1 - \gamma_j/\lambda_p)^{-1} \int_0^t \mathrm{d}t'\, e^{\gamma_i t'} [e^{-2(\lambda_p-\gamma_j)t'} - (\gamma_j/\lambda_p) e^{-2(\lambda_p-\gamma_j)t}] \frac{\partial^2}{\partial {x_j}^2} \langle\langle v_i(e^{-\mathbf{\Gamma}_0 t'}\cdot\mathbf{x}, t-t')\rangle\rangle \qquad (3.18)$$

The presence of the pole term $(1 - \gamma_i/\lambda_p)^{-1}$ is related to the onset of the coil–stretch transition of polymers in elongational flow when the largest strain rate ${\gamma_i}^{\max}$ approaches the smallest polymer relaxation rate, λ_1.[17] Notice that the force $\langle\langle \mathbf{F}\rangle\rangle$ is always parallel to the averaged velocity disturbance $\langle\langle \mathbf{v}\rangle\rangle$ and the different velocity components are not coupled by the influence of the polymer on the elongational flow field.

b. Planar Couette Flow. In the particular case of planar Couette (simple shear) flow, the transpose of the velocity gradient matrix is

$$\mathbf{\Gamma}_0 = \begin{pmatrix} 0 & \gamma & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad (3.19)$$

The fact that

$$\mathbf{\Gamma}_0\cdot\mathbf{\Gamma}_0 = \mathbf{\Gamma}_0^{\mathrm{T}}\cdot\mathbf{\Gamma}_0^{\mathrm{T}} = 0 \qquad (3.20)$$

can be used to expand the exponent in eq 3.8 and to obtain

$$\mathbf{g}(t) = \mathbf{1} + \mathbf{\Gamma}_0 t \qquad (3.21)$$

$$\mathbf{x}'(t') = [\mathbf{1} - \mathbf{\Gamma}_0(t-t')]\cdot\mathbf{x} \qquad (3.22)$$

and

$$\frac{\partial}{\partial \mathbf{x}'} = [\mathbf{1} + \mathbf{\Gamma}_0^{\mathrm{T}}(t-t')]\cdot\frac{\partial}{\partial \mathbf{x}} \qquad (3.23)$$

Substituting into eq 3.11–3.13 and using eq 3.21–3.23, after some algebraic manipulations we arrive at

$$\langle\langle F_i(\mathbf{x},t)\rangle\rangle = \rho \sum_{p=1}^{\infty} \int_0^t \mathrm{d}t'\, e^{-2\lambda_p t'} \left[\Delta + 2\gamma(t' + 1/2\lambda_p)\frac{\partial^2}{\partial x \partial y} + \gamma^2(t'^2 + t'/\lambda_p + 1/2{\lambda_p}^2)\frac{\partial^2}{\partial x^2}\right] [\langle\langle v_i(x-\gamma t' y, y, z, t-t')\rangle\rangle + \delta_{ix}\gamma t' \langle\langle v_y(x-\gamma t' y, y, z, t-t')\rangle\rangle] + \langle\langle F_i(\mathbf{x},t)\rangle\rangle_{\mathrm{tr}} \qquad (3.24)$$

where the transient contribution

$$\langle\langle F_i(\mathbf{x},t)\rangle\rangle_{\mathrm{tr}} = -\rho \sum_{p=1}^{\infty} (\gamma/\lambda_p) e^{-2\lambda_p t} \int_0^t \mathrm{d}t'\, e^{-2\lambda_p t'} \left[\frac{\partial^2}{\partial x \partial y} + \gamma(t + 1/2\lambda_p)\frac{\partial^2}{\partial x^2}\right] [\langle\langle v_i[x-\gamma(t-t')y, y, z, t')\rangle\rangle + \delta_{ix}\gamma t' \langle\langle v_y(x-\gamma(t-t')y, y, z, t')\rangle\rangle] \qquad (3.25)$$

vanishes in the long time limit, $\lambda_1 t \gg 1$, and can be neglected when considering the steady-state solutions to eq 2.36 and 3.24. Notice that unlike the case of elongational flow, the x-component of the polymer force on the fluid has a contribution from the y-component of the velocity field.

Equations 3.24 and 3.25 for planar Couette flow and eq 3.18 for elongational flow differ from the corresponding results presented in ref 5 and 6. The difference stems from the approximation $\langle \mathbf{B}\rangle\cdot\langle \mathbf{u}\rangle \approx \langle \mathbf{B}_0\rangle\cdot\langle \mathbf{u}\rangle$, where $\mathbf{B}_0$ is of zeroth order in $\mathbf{v}$, made in evaluating the polymer force on the fluid in eq 4.1 of ref 6. Terms such as $\langle \mathbf{B}_1\rangle\cdot\mathbf{v}_0$, where $\mathbf{B}_1$ is linear in $\mathbf{v}$, which are neglected in ref 5 and 6, appear in the present analysis.

3. Poiseuille (Pipe) Flow. As an example of a nonlinear applied velocity field we consider Poiseuille flow in a pipe, with

$$\mathbf{v}_0(\mathbf{x},t) = (G/4\eta_0)(a^2 - r^2)\hat{z} \qquad (3.26)$$

where G is the externally imposed pressure gradient, $\hat{z}$ is a unit vector in the direction of the applied flow (along the symmetry axis of the pipe), a is the radius of the pipe, and r measures the radial distance from the z axis. The velocity gradient tensor can be conveniently given in cylindrical coordinates (r,z,θ)

$$\boldsymbol{\Gamma}_0[\mathbf{x}(t),t] = -(G/2\eta_0)r\hat{z}\hat{r} \qquad (3.27)$$

Since r is determined by the initial conditions and does not change with time along the streamline, the velocity gradient tensor is time independent and consequently $\mathbf{g}$ is given by the exponential

$$\mathbf{g}(t) = e^{-(G/2\eta_0)rt\hat{z}\hat{r}} = 1 - (G/2\eta_0)rt\hat{z}\hat{r} \qquad (3.28)$$

Integrating eq 3.26, we obtain

$$\mathbf{x}(t) = \mathbf{x}(t') + (G/4\eta_0)(t - t')(a^2 - r^2)\hat{z} \qquad (3.29)$$

and

$$\frac{\partial}{\partial \mathbf{x}} = [1 + (G/2\eta_0)(t - t')r\hat{r}\hat{z}]\cdot\frac{\partial}{\partial \mathbf{x}'} = \frac{\partial}{\partial \mathbf{x}'}\cdot[1 + (G/2\eta_0)(t - t')r\hat{z}\hat{r}] \qquad (3.30)$$

Substituting (3.28)–(3.30) into (2.42)–(2.45) gives the following expression for the average polymer force on the fluid

$$\langle\langle \mathbf{F}(\mathbf{x},t)\rangle\rangle = \rho\sum_{p=1}^{\infty} e^{-2\lambda_p t}\frac{\partial}{\partial \mathbf{x}}\cdot\left\{\left[1 - \int_0^t \mathrm{d}t'\,\langle\langle v_r(\mathbf{x}',t')\rangle\rangle\frac{\partial}{\partial r}\right]\times [\mathbf{g}(t)\cdot\boldsymbol{\Lambda}(p,t)\cdot\mathbf{g}^{\mathrm{T}}(t)] + \int_0^t \mathrm{d}t'\,\mathbf{g}(t)\cdot[\boldsymbol{\mu}(t')\cdot\boldsymbol{\Lambda}(p,t') + \boldsymbol{\Lambda}(p,t')\cdot\boldsymbol{\mu}^{\mathrm{T}}(t')]\cdot\mathbf{g}^{\mathrm{T}}(t)\right\} \qquad (3.31)$$

where we have used the observation that the elements of the tensor

$$\boldsymbol{\Lambda}(p,t) = e^{2\lambda_p t}\mathbf{1} + (G/2\eta_0)(r/2\lambda_p)[e^{2\lambda_p t}(2\lambda_p t - 1) + 1](\hat{r}\hat{z} + \hat{z}\hat{r}) + 2(G/2\eta_0)^2(r/2\lambda_p)^2[e^{2\lambda_p t}(2\lambda_p{}^2t^2 - 2\lambda_p t + 1) - 1]\hat{z}\hat{z} \qquad (3.32)$$

depend only on the spatial coordinate r and where

$$\boldsymbol{\mu}^{\mathrm{T}}(t') = \frac{\partial}{\partial \mathbf{x}'}\langle\langle \mathbf{v}(\mathbf{x}',t')\rangle\rangle + (G/2\eta_0)rt'\left[\frac{\partial}{\partial \mathbf{x}'}\langle\langle v_r(x',t')\rangle\rangle\hat{z} - \frac{\partial}{\partial z'}\hat{r}\langle\langle \mathbf{v}(\mathbf{x}',t')\rangle\rangle\right] - \left[(G/2\eta_0)^2(rt')^2\frac{\partial}{\partial z'}\langle\langle v_r(\mathbf{x}',t')\rangle\rangle + (G/2\eta_0)\int_0^{t'}\mathrm{d}t''\,\langle\langle v_r(\mathbf{x}'',t'')\rangle\rangle\right]\hat{r}\hat{z} \qquad (3.33)$$

Unforuntately, the above equations cannot be further simplified without introducing some assumptions about the functional dependence of the solution velocity profile.

4. Discussion

We present the derivation of the linear, partial integrodifferential equations that govern the large-scale hydrodynamics of dilute polymer solutions subjected to arbitrary externally imposed boundary and initial conditions. To the best of our knowledge, these results have never been presented before.[18] More explicit (in terms of the polymer and applied flow parameters) expressions for the hydrodynamic equations are given for weak, elongational, planar Couette, and Poiseuille (applied) flows. We believe that this model captures the essentials of the physical mechanisms responsible for the viscous dissipation and elastic memory effects in dilute flowing polymer solutions and that its investigation will provide valuable insights about the foundations of nonlinear viscoelasticity and non-Newtonian fluid mechanics. The numerical analysis of its consequences for several concrete flow situations is the subject of current work. An analytical approach, based on the recent results of ref 19, is also being considered. While the solution of our hydrodynamic equations automatically gives the solvent velocity gradient tensor-type contribution (missing from constitutive equation-type models[3]) to the total stress tensor, the effect on the material functions measured in traditional rheological experiments is small since it is of second order in polymer concentration. Strong effects on polymer hydrodynamics are expected in situations involving flow instabilities since the presence of polymers can perturb the balance between viscious dissipation and inertial transfer.[26] Consequently, a direct test of the theory will have to involve a new generation of high-resolution experiments capable of measuring the local velocity[20] and velocity gradient[21] profiles in dilute flowing polymer solutions.

We conclude with several comments on the limits of validity and on the approximations involved in our theory. An obvious limitation is associated with the use of an elastic (Gaussian) model for the polymer chain that is known to break down in elongational flow when the strain rate exceeds the inverse of the longest polymer relaxation time[22] (coil–stretch transition). The generalization of our model to account for the finite extensibility of the polymer chains is prohibitively difficult, unless restriction is made to an oversimplified single-mode description of the macromolecule (such as the finitely extensible nonelastic dumbbell model[1]). Fortunately, these inelastic effects are not expected to play a dominant role in other rheologically important flows (planar Couette etc.) where the rotation of the fluid elements tends to limit the polymer extension even in the limit of very high velocity gradients.[21]

A deeper issue is related to our separation of the velocity field into microscopic and macroscopic components. Following the renormalization group studies of intrapolymer hydrodynamic interactions in the absence of applied flow,[16,23] we assume that the microscopic velocity field renormalizes the polymer relaxation rates; the free-draining rates are thus replaced by their hydrodynamically "dressed" counterparts and the "dressed" polymer affects the macroscopic velocity field in the manner described in this work. This still leaves open the question of whether the "dressing" of the relaxation rates by the hydrodynamic interactions is affected by the applied velocity gradients. While the renormalization group analysis of ref 24 appears to suggest that, at least perturbatively (to second order in the velocity gradients), the polymer relaxation spectrum is only affected by the local hydrodynamic interactions between the monomers and is not sensitive to macroscopic flow, the "consistent averaging" approach[25] finds that the polymer spectrum is modified in the presence of strong applied shear flow. Further renormalization group studies dealing with this question are now under way.

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Appendix

We want to evaluate the averages over the three tensors that appear in eq 2.39 and 2.41. The first one is

$$\chi^{(00)} \equiv \int_0^N \mathrm{d}\tau \left\langle \frac{\partial^2 \mathbf{r}_0(\tau,t)}{\partial \tau^2} \mathbf{r}_0(\tau,t) \right\rangle \tag{A.1}$$

Substituting eq 2.28 for $\mathbf{r}_0(\tau,t)$ we get

$$\begin{aligned} \chi_{ij}{}^{(00)} = \sum_{k,l=1}^{3} g_{ik}(t) g_{jl}(t) \times \\ \int_0^N \mathrm{d}\tau \int_0^N \mathrm{d}\tau' \int_0^N \mathrm{d}\tau'' \left\{ \frac{\partial^2 G_0(\tau,\tau'|t)}{\partial \tau^2} G_0(\tau,\tau''|t) \times \right. \\ \langle r_k(\tau') r_l(\tau'') \rangle + \int_0^t \mathrm{d}t' \int_0^{t'} \mathrm{d}t'' \, [\mathbf{g}^{-1}(t')]_{km} [\mathbf{g}^{-1}(t'')]_{ln} \times \\ \left. \frac{\partial^2 G_0(\tau,\tau'|t-t')}{\partial \tau^2} G_0(\tau,\tau''|t-t'') \langle \theta_m(\tau',t') \theta_n(\tau'',t'') \rangle \right\} \end{aligned} \tag{A.2}$$

From eq 2.4, the relation

$$\langle r_k(\tau') r_l(\tau'') \rangle = \delta_{kl} \min\,(\tau',\tau'') \tag{A.3}$$

and the definition of G_0 (eq 2.29), the integrations in eq A.2 are performed. A straightforward calculation gives

$$\begin{aligned} \chi^{(00)} = -\sum_{p=1}^{\infty} e^{-2\lambda_p t} \Big\{ \mathbf{g}(t)\cdot\mathbf{g}^{\mathrm{T}}(t) + \\ 2\lambda_p \int_0^t \mathrm{d}t' \, \mathrm{e}^{2\lambda_p t'} \mathbf{g}(t)\cdot\mathbf{g}^{-1}(t')\cdot[\mathbf{g}(t)\cdot\mathbf{g}^{-1}(t')]^{\mathrm{T}} \Big\} \end{aligned} \tag{A.4}$$

Similarly, substituting eq 2.32 for $\mathbf{r}_1(\tau,t)$ and using the decoupling approximation, eq 2.38, we obtain

$$\begin{aligned} \chi_{ij}{}^{(10)} \equiv \int_0^N \mathrm{d}\tau \left\langle \frac{\partial^2 r_{1i}(\tau,t)}{\partial \tau^2} r_{0j}(\tau,t) \right\rangle = \sum_{k=1}^{3} \int_0^t \mathrm{d}t' \\ \left\{ \mathbf{g}(t)\cdot\mathbf{g}^{-1}(t')\cdot \left[\langle\langle \boldsymbol{\Gamma}_1(t') \rangle\rangle + \langle\langle \mathbf{R}_1(t') \rangle\rangle \cdot \frac{\partial}{\partial \mathbf{x}'} \boldsymbol{\Gamma}_0(t') \right] \right\}_{ik} \times \\ \int_0^N \mathrm{d}\tau \int_0^N \mathrm{d}\tau' \, \frac{\partial^2 G_0(\tau,\tau'|t-t')}{\partial \tau^2} \langle r_{0k}(\tau',t') r_{0j}(\tau t) \rangle \end{aligned} \tag{A.5}$$

Introducing eq 2.28 for $\mathbf{r}_0(\tau,t)$ enables the evaluation of the integrals

$$\begin{aligned} \int_0^N \mathrm{d}\tau \int_0^N \mathrm{d}\tau' \, \frac{\partial^2 G_0(\tau,\tau'|t-t')}{\partial \tau^2} \langle r_{0k}(\tau',t') r_{0j}(\tau,t) \rangle = \\ \sum_{m,n=1}^{3} \int_0^N \mathrm{d}\tau \int_0^N \mathrm{d}\tau' \int_0^N \mathrm{d}\sigma \int_0^N \mathrm{d}\sigma' \, \frac{\partial^2 G_0(\tau,\tau'|t-t')}{\partial \tau^2} \times \\ \{ g_{km}(t') g_{jn}(t) G_0(\tau',\sigma'|t') G_0(\tau,\sigma|t) \langle r_m(\sigma') r_n(\sigma) \rangle + \\ \int_0^t \mathrm{d}s \int_0^{t'} \mathrm{d}s' \, [\mathbf{g}(t')\cdot\mathbf{g}^{-1}(s')]_{km} [\mathbf{g}(t)\cdot\mathbf{g}^{-1}(s)]_{jn} \times \\ G_0(\tau',\sigma'|t'-s') G_0(\tau,\sigma|t-s) \langle \theta_m(\sigma',s') \theta_n(\sigma,s) \rangle \} \end{aligned} \tag{A.6}$$

The calculation is simplified by using the identity

$$\int_0^N \mathrm{d}\tau' \, \frac{\partial^2 G_0(\tau,\tau'|t)}{\partial \tau^2} G_0(\tau',\sigma|t') = \frac{\partial^2 G_0(\tau,\sigma|t+t')}{\partial \tau^2} \tag{A.7}$$

and, after performing the integrations over time and polymer contour variables, we get

$$\begin{aligned} \chi^{(10)} = -\sum_{p=1}^{\infty} e^{-2\lambda_p t} \int_0^t \mathrm{d}t' \, \mathbf{g}(t)\cdot\mathbf{g}^{-1}(t')\cdot \Big[\langle\langle \boldsymbol{\Gamma}_1(t') \rangle\rangle + \\ \langle\langle \mathbf{R}_1(t') \rangle\rangle \cdot \frac{\partial}{\partial \mathbf{x}'} \boldsymbol{\Gamma}_0(t') \Big] \cdot \Big\{ \mathbf{g}(t')\cdot\mathbf{g}^{\mathrm{T}}(t) + \\ 2\lambda_p \int_0^{t'} \mathrm{d}s \, e^{2\lambda_p s} \mathbf{g}(t')\cdot\mathbf{g}^{-1}(s)\cdot[\mathbf{g}(t)\cdot\mathbf{g}^{-1}(s)]^{\mathrm{T}} \Big\} \end{aligned} \tag{A.8}$$

The calculation of

$$\chi^{(01)} = \int_0^N \mathrm{d}\tau \left\langle \frac{\partial^2 \mathbf{r}_0(\tau,t)}{\partial \tau^2} \mathbf{r}_1(\tau,t) \right\rangle \tag{A.9}$$

proceeds along the same lines to produce

$$\chi^{(01)} = [\chi^{(10)}]^{\mathrm{T}} \tag{A.10}$$

Substituting the above expressions in eq 2.41 yields the stress tensor, eq 2.42.

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