Low-shear viscosity of nondilute polymer solutions from a generalized Kirkwood-Riseman model

1 AUTHOR:

George Phillies
Worcester Polytechnic Institute
193 PUBLICATIONS   **3,370** CITATIONS

Low-Shear Viscosity of Non-Dilute Polymer Solutions From a Generalized Kirkwood-Riseman Model

George D. J. Phillies*

Professor Emeritus, Department of Physics, Worcester Polytechnic Institute,Worcester, MA 01609

The low shear viscosity η of a non-dilute polymer solution is calculated from an extended Kirkwood-Riseman model that includes hydrodynamic interactions between chains. Hydrodynamic interaction tensors for chains in a weak shear field are obtained for interacting pairs and trios of chains. The model proposed here gives a general expansion for $\eta(c)$ to arbitrary order in polymer concentration c. Divergent integrals encountered in some prior calculations using Stokes-level hydrodynamics are avoided. The model confirms empirical demonstrations that the intrinsic viscosity $[\eta]$ is a good reducing variable for $\eta(c)$.

I.   INTRODUCTION

The nature of polymer dynamics in non-dilute polymer solutions remains a fundamental problem for the theory of complex fluids. For entirely dilute solutions, the hydrodynamic model of Kirkwood and Riseman[1] appears to provide approximate answers. In non-dilute solutions, interactions between polymer chains not included in the dilute-solution Kirkwood-Riseman model should play a major role in polymer dynamics.

In two previous papers[2, 3], I proposed extending the Kirkwood-Riseman model to include interchain hydrodynamics. The extension had four main assumptions:

(i) The dominant force between polymer chains is hydrodynamic, chain-crossing constraints providing secondary corrections.

(ii) Hydrodynamic interactions between polymers can be approximated by a direct extension of the Kirkwood-Riseman[1] bead- spring model to include hydrodynamic couplings between beads on distinct chains.

(iii) Assumptions (i) and (ii) yield a pseudovirial concentration expansion for transport coefficients.

(iv) The Altenberger-Dahler Positive Function Renormalization Group[4, 5] and appropriate inputs for the concentration dependence of equilibrium properties allow one to extrapolate (iii) to elevated concentrations.

The previous papers[2, 3] treated the polymer self- diffusion coefficient D_s, predicting the functional dependence of D_s on concentration c and the dependence of the parameters of $D_s(c)$ on polymer molecular weight M. Those predictions[2, 3] are in good agreement with the experimental literature on D_s. However, these previous papers focused on one transport parameter. Agreement between experiment and theory might be an accident that remained undetected because only one phenomenological property was examined.

Here the same approach is used to calculate the concentration dependence of the low-shear viscosity. This paper obtains a pseudovirial series for $\eta(c)$ and confirms the convergence of individual terms. Intrachain hydrodynamics are modeled in a simplified manner. Underlying hydrodynamic interactions depend on interchain distance as r^{-2} and r^{-3}; convergence is nontrivial. The computation of adequate higher-order pseudovirial coefficients to apply PFRG methods is postponed to a later paper.

Treatments of $\eta(c)$ in the literature include a series[6]-[9] of papers dating to the early 1950's, studies a decade later by Yamakawa[10] and by Peterson and Fixman[11], and more recent results by Freed and Edwards[12]-[14] and Freed and Perico[15]. Brinkman[6] obtained $\eta(c)$ by considering the effect on η of adding a single sphere, the solution being treated as a continuum with dressed viscosity $\eta(c)$. Riseman and Ullman[7] computed along lines physically similar to this paper the intermolecular hydrodynamic interactions of polymer chains. However, ref. [7] calculated the effect of interchain interactions on the velocity gradient du_y/dx and inferred therefrom the viscosity.

Saito[8] evaluated the second-order concentration correction to η by examining self-consistently how polymers throughout the solution reduce the average shear $\langle \kappa \rangle$ acting on a polymer at the origin. Saito noted that the integrals for $\langle \kappa \rangle$ were improper; their value depended on the order of integration. Saito[9] later proposed that the improper integrals arose because the underlying interaction depended on interchain distance as r^{-2}. These range

---

*Electronic address: `phillies@4liberty.net`

issues arose because hydrodynamic forces were treated with the Stokes approximation, which neglects fluid inertia. Saito proposed that divergences would vanish if the Stokes approximation were replaced by the Oseen approximation (not to be confused with the Oseen tensor). However, a calculation of $\eta(c)$ based on the Oseen approximation has not been reported, so Saito's[9] proposal is not yet confirmed by explicit calculation.

Yamakawa[10] re-examined a part of the second-order concentration dependence, namely the part arising because the radius of a polymer decreases as c increases. Yamakawa's effect is critical if $\eta(c)$ is to be examined for polymers of given molecular weight rather than given hydrodynamic radius, but other effects also contribute to $\eta(c)$.

Peterson and Fixman[11] review past efforts to calculate the Huggins coefficient k_H of

$$\eta/\eta_o = 1 + [\eta]c + k_H[\eta]^2 c^2 \tag{1}$$

A wide variety of results have been reported. Here η_o is the solvent viscosity, $[\eta]$ is the intrinsic viscosity, and c is the polymer concentration. Phenomenologically, k_H is ≈ 0.3 in good solvents and ≈ 0.6 in theta solvents[18, 19]. Eq. 1 defines k_H, so it gives no evidence that $[\eta]$ is a good reducing variable for the series. Identifying the primary difficulty in calculations as the long- range nature of hydrodynamic interactions, Peterson and Fixman propose that computing k_H is analogous to computing constitutive coefficients in macroscopic electrodynamics. The response of a dielectric body to an external electric field reflects not only its microscopic properties but also its shape and induced surface charges, but by computing self-consistently the local fields and the polarizations one obtains a shape-independent local dielectric constant without needing to treat the shape of the object. By computing simultaneously the average stress tensor and the average velocity gradient Peterson and Fixman estimated k_H without treating boundary stresses.

Freed and Edwards[12–14] proposed a general treatment of polymer hydrodynamics, and predicted k_H. Freed and Edwards report that their procedures do not involve improper integrals, because–according to Freed and Edwards–"by analogy with the Debye screening in Coulomb systems, we showed how hydrodynamic interactions become screened in concentrated polymer solutions." Later papers by Freed and Perico[15] and Altenberger, et al.[16] come to a different conclusion from a similar model, finding that hydrodynamic screening does not arise at low frequencies for polymer chains that are free to move with respect to each other. However, However, if there were no hydrodynamic screening for freely moving chains, then why are the integrals for k_H convergent? This paper provides a non-unique answer to this problem.

This paper has six Sections. In Section II, a generalized Kirkwood-Riseman model of polymer hydrodynamics gives a complete iterative scheme for computing multi-chain hydrodynamic interactions for polymers in a shear field. Section III develops a general form for $\eta(c)$ in terms of averages over these tensors. Section IV computes the average shear. Section V obtains $\eta(c)$ through $\mathcal{O}(c^2)$ and treats short- and long-range convergence issues. Section VI presents conclusions.

II. HYDRODYNAMIC INTERACTIONS OF NON-OVERLAPPING POLYMER CHAINS

This Section considers hydrodynamic interactions between polymers in a weak hydrodynamic shear field. By 'weak', it is here meant that the shear is so small that chain conformations are not significantly perturbed. In a weak shear the polymer radius of gyration R_g and hydrodynamic radius R_h retain their equilibrium values.

Chains are described by the Kirkwood-Riseman bead-spring model. A chain is a line of beads that interacts hydrodynamically by applying point forces to the solvent. The solvent responds to point forces via the time-independent Oseen tensor. Beads on a single chain are linked by springs, springs being hydrodynamically inert couplers that keep the beads of a chain from diffusing away from each other. The description of the springs and beads could be refined to add interactions between nonadjacent beads. Here internal chain dynamics are effectively suppressed; only whole-chain translations and rotations are taken into account.

Hydrodynamic interactions between beads follow the Oseen tensor

$$\mathbf{T}(\mathbf{r}) = \frac{1}{8\pi\eta_o r}[\mathbf{I} + \hat{\mathbf{r}}\hat{\mathbf{r}}] \tag{2}$$

which gives the fluid flow $\mathbf{u}$ at location $\mathbf{r}$ relative to the location at which a point force $\mathbf{F}$ is applied, via

$$\mathbf{u}(\mathbf{r}) = \mathbf{T}(\mathbf{r}) \cdot \mathbf{F}. \tag{3}$$

Here $\mathbf{I}$ is the unit tensor, $r = |\mathbf{r}|$, the unit vector is $\hat{\mathbf{r}} = \mathbf{r}/r$, η_o is the solvent viscosity, and $\hat{\mathbf{r}}\hat{\mathbf{r}}$ is an outer product. The force $\mathbf{F}$ on the solvent due to a bead is

$$\mathbf{F}_i = f_i(\mathbf{v}_i - \mathbf{u}(\mathbf{r}_i)), \tag{4}$$

where f_i is the drag coefficient for bead i, $\mathbf{r}_i$ and $\mathbf{v}_i$ are the position and velocity of bead i with respect to the system coordinates, and $\mathbf{u}(\mathbf{r}_i)$ is the velocity that the solvent would have had at $\mathbf{r}_i$ if the bead were absent.

Interchain hydrodynamic interactions are computed via the method of reflections: A chain moving with respect to the solvent induces solvent flows. These flows act on other chains, causing the other chains to move and inducing further 'scattered' solvent flows. The imposed solvent flow is denoted $\mathbf{u}^{(0)}$. Solvent flows due to scattering by the first, second,... chains in a sequence are denoted $\mathbf{u}^{(1)}$, $\mathbf{u}^{(2)}$, ..., respectively. The total flow at $\mathbf{r}_i$ is

$$\mathbf{u}(\mathbf{r}_i) = \sum_n \mathbf{u}^{(n)}(\mathbf{r}_i). \tag{5}$$

For notational clarity, this section considers a scattering sequence from a chain 1 to a chain 2 to a chain 3, etc. The total single-scattered field at chain 2 is the sum of the single-scattered fields due to every other chain. Notation for the total scattered field is in Section III. A full Kirkwood- Riseman model would include intrachain as well as interchain hydrodynamic interactions. Here intrachain interactions are incorporated via an approximation given below.

The positions of the chain centers of mass relative to the coordinate origin are denoted $\mathbf{a}_j$, the j labelling which of the N_c chains is involved. Labelling the chains that generate a series of reflections 1, 2, 3, ..., vectors $\mathbf{R_1}$, $\mathbf{R_2}$, ... give, respectively, the center-of-mass location of chain 2 with respect to the center of mass of chain 1, of chain 3 with respect to chain 2, ..., so that $\mathbf{R}_j = \mathbf{a}_{j+1} - \mathbf{a}_j$. The location of a bead i with respect to its chain's center-of-mass is $\mathbf{s}_i$. The following only refers at one time to beads on a single chain, so $\mathbf{s}_i$ does not need a label identifying its chain.

The velocity $\mathbf{v}_j$ of bead j of chain i may be written

$$\mathbf{v}_j = \mathbf{V}^{(i)} + \mathbf{\Omega}^{(i)} \times \mathbf{s}_j + \dot{\mathbf{w}}_j. \tag{6}$$

Here $\mathbf{V}^{(i)}$ is the chain's center-of-mass velocity, $\mathbf{\Omega}^{(i)}$ is the chain's angular velocity around its center of mass, and $\dot{\mathbf{w}}_i$ represents the component of the bead velocity arising from chain internal modes.

$\mathbf{V}$ and $\mathbf{\Omega}$ carry superscripts identifying reflections. The initial fluid velocity $\mathbf{u}^{(0)}$ induces velocities $\mathbf{V}^{(1)}$ and $\mathbf{\Omega}^{(1)}$ in the first chain. The first chain creates a reflected flow $\mathbf{u}^{(1)}$ that gives a second chain velocities $\mathbf{V}^{(2)}$ and $\mathbf{\Omega}^{(2)}$, etc.

The chain center-of-mass velocity is

$$\mathbf{V}^{(i)} = \frac{\partial \mathbf{a}_i}{\partial t}. \tag{7}$$

It is determined by averaging over the N beads of chain i as

$$\mathbf{V}^{(i)} = \frac{1}{N} \sum_{j=1}^{N} \mathbf{v}_j. \tag{8}$$

The $\mathbf{V}^{(i)}$ and $\dot{\mathbf{w}}_i$ are independent of $\mathbf{\Omega}^{(i)}$, so $\mathbf{\Omega}^{(i)}$ can be determined from

$$\frac{1}{N} \sum_{j=1}^{N} \mathbf{s}_j \times (\mathbf{\Omega}^{(i)} \times \mathbf{s}_j) = \frac{1}{N} \sum_{j=1}^{N} \mathbf{s}_j \times \mathbf{v}_j. \tag{9}$$

Here the instantaneous-square chain radius s^2 is $N^{-1} \sum_{j=1}^{N} s_j^2$.

This paper is limited to the low-frequency regime. Inertial effects are neglected, so fluctuations in the chain linear and angular momenta average to zero. Couplings between fluid flows and the higher-frequency $\dot{\mathbf{w}}_i$ are neglected. Chain motions are therefore subject to constraints: The total force and total torque on each chain approximately vanish, namely

$$-\sum_{j=1}^{N} f_j(\mathbf{v}_j - \mathbf{u}(\mathbf{r}_j)) = 0 \tag{10}$$

and

$$-\sum_{j=1}^{N} \mathbf{s}_j \times f_j(\mathbf{v}_j - \mathbf{u}(\mathbf{r}_j)) = 0 \tag{11}$$

Eqs. 8, 9, 10 and 11 determine the chain center-of-mass translational and rotational velocities $\mathbf{V}^{(n)}$ and $\mathbf{\Omega}^{(n)}$ in terms of the fluid velocity $\mathbf{u}^{(n-1)}(\mathbf{r}_j)$ at the beads of chain n. The $\mathbf{V}^{(n)}$ and $\mathbf{\Omega}^{(n)}$ depend on the relative chain positions.

To establish a clear format for future work, this paper omits intrachain hydrodynamics. An effective drag coefficient for each bead replaces more detailed hydrodynamic interactions. All sums $\sum_j f_j$ over beads are replaced with integrals $\int ds g(\mathbf{s}) f(\mathbf{s})$, $\mathbf{s}$ being a vector from the chain center of mass to a point within the chain, $g(\mathbf{s})$ being the density of beads at $\mathbf{s}$, and $f(\mathbf{s})$ being the effective drag coefficient of beads at $\mathbf{s}$. The integral of $f(\mathbf{s})$ over all beads of a chain is the drag coefficient F_o. Refinement of this approximation is left for a subsequent paper. All functions of the bead label are replaced by functions of $\mathbf{s}$. Ensemble averages over chain configurations refer to isolated chains; correlations in configurations of nearby chains are neglected.

To describe the solvent flow within chain $n + 1$, $\mathbf{u}^{(n)}$ is Taylor-expanded around the center of mass of chain $n + 1$, the expansion being

$$\mathbf{u}^{(n)}(\mathbf{R}_n + \mathbf{s}) = \mathbf{u}^{(n)}(\mathbf{R}_n) + (\mathbf{s} \cdot \nabla)\mathbf{u}^{(n)}(\mathbf{R}_n) + \frac{1}{2}(\mathbf{s} \cdot \nabla)^2 \mathbf{u}^{(n)}(\mathbf{R}_n) + \ldots, \tag{12}$$

In practice, terms above first order in $\mathbf{s}$ are not needed. The $\mathbf{u}^{(n)}$ are implicit functions of $\mathbf{a}_1$ and the $\mathbf{R}_j$ with $j < n$.

We start with a chain in a non-uniform solvent flow. If the imposed flow is $u_y^{(0)}(\mathbf{r})\hat{\mathbf{j}}$, the shear is

$$\frac{\partial u_y^{(0)}(\mathbf{r})}{\partial x}\hat{\mathbf{j}} = \alpha(x)\hat{\mathbf{j}}. \tag{13}$$

$(\hat{\mathbf{i}}, \hat{\mathbf{j}}, \hat{\mathbf{k}})$ being Cartesian-axis unit vectors. The Oseen tensor is long-range. To avoid complications related to system boundaries, the imposed velocity field is given a sinusoidal spatial dependence with wavevector k:

$$\mathbf{u}^{(0)}(\mathbf{r}) = u_0 \cos(kx)\hat{\mathbf{j}}, \tag{14}$$

The oscillations in space are non-propagating, so $\alpha(x) = -u_0 k \sin(kx)$. The average shear is $u_0^2 k^2 / 2 \equiv \langle \alpha^2 \rangle$. As discussed in Section IV, the imposed $\mathbf{u}^0$ is the bare shear field, not the dressed shear field measured experimentally. If the chains are sufficiently small that $\cos(kx)$ does not vary substantially over the extent of a polymer chain, and the low-k limit is taken by keeping $u_0 k$ constant, the linear viscosity increment should be insensitive to k. The limit $k \to 0$ is taken after the ensemble average over chain positions. The limit $k \to 0$ and the integrals of the ensemble average can not in general be exchanged.

The above is now applied to calculate the motions of a series of chains in a shear field, with $\mathbf{u}^{(0)}$ given by eq. 14. The first chain is treated explicitly. General formulae are obtained for all further chains.

For the first chain, the zero-force condition is

$$\int d\mathbf{s} f(\mathbf{s}) g(\mathbf{s})(\mathbf{v}^{(1)}(\mathbf{s}) - \mathbf{u}^{(0)}(\mathbf{s})) = 0 \tag{15}$$

Writing $\mathbf{v}$ in terms of chain coordinates via eq. 6, a Taylor expansion of the fluid velocity around the chain center of mass (with $s_x = \mathbf{s} \cdot \mathbf{i}$ and $a_x = \mathbf{a}_1 \cdot \mathbf{i}$), gives

$$\int d\mathbf{s} f(\mathbf{s}) g(\mathbf{s}) \left(\mathbf{V}^{(1)} + \mathbf{\Omega}^{(1)} \times \mathbf{s} + \dot{\mathbf{w}}(\mathbf{s}) - u_0 \cos(ka_x)\hat{\mathbf{j}} - \alpha(a_x)s_x\hat{\mathbf{j}} - \frac{1}{2}(\mathbf{s} \cdot \nabla)^2 \mathbf{u}^{(0)}(\mathbf{a}_1) - \ldots \right). \tag{16}$$

The weak shear condition assures that $f(\mathbf{s})g(\mathbf{s})$ has spherical symmetry, so terms that are odd in $\mathbf{s}$ vanish. Internal relaxations are neglected, leading to

$$\mathbf{V}^{(1)} = u_0 \cos(ka_x)\hat{\mathbf{j}} + \mathcal{O}(s^2) \tag{17}$$

Up to $\mathcal{O}(s^2)$ corrections, the chain drifts with the velocity that the solvent would have had, at the chain's center of mass location, if the chain were absent.

The zero-torque condition leads to the first chain's rotational velocity. Eq. 11 becomes

$$\int d\mathbf{s} f(\mathbf{s}) g(\mathbf{s}) \mathbf{s} \times (\mathbf{v}^{(1)}(\mathbf{s}) - \mathbf{u}^{(0)}(\mathbf{s})) = 0. \tag{18}$$

Substituting for $\mathbf{v}^{(1)}$ and $\mathbf{u}^{(0)}$,

$$\int d\mathbf{s} f(\mathbf{s}) g(\mathbf{s}) \mathbf{s} \times (\mathbf{V}^{(1)} + \mathbf{\Omega}^{(1)} \times \mathbf{s} + \dot{\mathbf{w}})$$

$$= \int d\mathbf{s} f(\mathbf{s})g(\mathbf{s})[\mathbf{s} \times (u_0 \cos(ka_x)\hat{\mathbf{j}} - \alpha(a_x)s_x\hat{\mathbf{j}} - \frac{1}{2}(\mathbf{s} \cdot \nabla)^2\mathbf{u}^{(0)}(\mathbf{s}) - \ldots)] \tag{19}$$

Symmetry again eliminates terms odd in $\mathbf{s}$. Denoting $\int d\mathbf{s} f(\mathbf{s})g(\mathbf{s})Q(\mathbf{s}) = F_o\langle Q(\mathbf{s})\rangle$, one has $\langle \mathbf{s} \cdot \mathbf{s}\rangle = F_o S^2$, $\langle s_x^2\rangle = F_o S^2/3$, and $\langle s_i s_j\rangle = 0$ for $i \neq j$, s_j being the jth component of $\mathbf{s}$. Component-by-component analysis reveals identities for averages over $\mathbf{s}$, including $\langle (\mathbf{s} \cdot \mathbf{a})\mathbf{s}\rangle = F_o \mathbf{a} S^2/3$, $\langle (\mathbf{s} \cdot \mathbf{a})(\mathbf{s} \cdot \mathbf{b})\rangle = F_o \mathbf{a} \cdot \mathbf{b} S^2/3$, $\langle \mathbf{s} \times \hat{\mathbf{j}} s_x\rangle = F_o \hat{\mathbf{k}} S^2/3$, and $\langle (\mathbf{s} \cdot \mathbf{a})(\mathbf{s} \times \mathbf{b})\rangle = F_o \mathbf{a} \times \mathbf{b} S^2/3$, where $\mathbf{a}$ and $\mathbf{b}$ are constant vectors.

Applying these identities and $\mathbf{a} \times (\mathbf{b} \times \mathbf{c}) = (\mathbf{a} \cdot \mathbf{c})\mathbf{b} - (\mathbf{a} \cdot \mathbf{b})\mathbf{c}$, one finds

$$\langle \mathbf{s} \times (\mathbf{\Omega} \times \mathbf{s})\rangle = \frac{2}{3}S^2\mathbf{\Omega}. \tag{20}$$

Eq. 19 reduces to

$$\mathbf{\Omega}^{(1)} = \frac{\alpha}{2}\hat{\mathbf{k}}, \tag{21}$$

in agreement with the single-chain result of Kirkwood and Riseman[1].

The translational and rotational velocities of the first chain in a scattering series are now established. Chain 1 cannot be entirely stationary — with respect to the solvent — at every point along its length, so it exerts forces on the solvent. These forces induce a new solvent flow $\mathbf{u}^{(1)}$ representing scattering of $\mathbf{u}^{(0)}$ by chain 1.

For the flow induced at $\mathbf{r}$ by chain 1, eq. 3 gives

$$\mathbf{u}^{(1)}(\mathbf{r}) = \int d\mathbf{s} f(\mathbf{s})g(\mathbf{s})\mathbf{T}(\mathbf{r} - \mathbf{s}) \cdot (\mathbf{v}^{(1)}(\mathbf{s}) - \mathbf{u}^{(0)}(\mathbf{s})). \tag{22}$$

A Taylor-series expansion of the Oseen tensor is

$$\mathbf{T}(\mathbf{r} - \mathbf{s}) = \mathbf{T}(\mathbf{r}) - \mathbf{s} \cdot \nabla\mathbf{T}(\mathbf{r}) + \mathcal{O}(s^2) \tag{23}$$

where

$$\mathbf{s} \cdot \nabla\mathbf{T}(\mathbf{r}) = \frac{1}{8\pi\eta_o}\left(\frac{\mathbf{s}\hat{\mathbf{r}}}{r^2} + \frac{\hat{\mathbf{r}}\mathbf{s}}{r^2} - \frac{\mathbf{s} \cdot \hat{\mathbf{r}}}{r^2}(\mathbf{I} + 3\hat{\mathbf{r}}\hat{\mathbf{r}})\right). \tag{24}$$

On substituting in eq. 22 for $\mathbf{T}$, $\mathbf{V}^{(1)}$, and $\mathbf{u}^{(0)}$, the induced flow is

$$\mathbf{u}^{(1)}(\mathbf{r}) = \int d\mathbf{s} f(\mathbf{s})g(\mathbf{s})(\mathbf{T}(\mathbf{r}) - \mathbf{s} \cdot \nabla\mathbf{T}(\mathbf{r}) + \mathcal{O}(s^2)) \cdot (u_0 \cos(ka_x)\hat{\mathbf{j}} + \frac{\alpha}{2}\mathbf{k} \times \mathbf{s} + \dot{\mathbf{w}} - u_0 \cos(ka_x)\hat{\mathbf{j}} - \alpha s_x\hat{\mathbf{j}}). \tag{25}$$

Symmetry again eliminates terms odd in $\mathbf{s}$. The chain translation velocity cancels the fluid velocity at the center of mass. Identities for integrals over $\mathbf{s}$ lead to

$$\mathbf{u}^{(1)}(\mathbf{r}) = \frac{F_o \alpha S^2}{8\pi\eta_o r^2}\frac{xy}{r^2}\hat{\mathbf{r}}. \tag{26}$$

Velocities of further chains and their scattered flows follow algorithmically. For the nth flow field and its action on the $(n+1)^{\text{th}}$ particle, on comparison with eqs. 15 and 16, and expanding $\mathbf{u}^{(n)}(\mathbf{R}_n + \mathbf{s})$ around $\mathbf{R}_n$, the zero-force condition is

$$\int d\mathbf{s} f(\mathbf{s})g(\mathbf{s})\left(\mathbf{V}^{(n+1)} + \mathbf{\Omega}^{(n+1)} \times \mathbf{s}_j + \dot{\mathbf{w}} - \mathbf{u}^{(n)}(\mathbf{R}_n) - \mathbf{s} \cdot \nabla(\mathbf{u}^{(n)}(\mathbf{R}_n)) - \frac{1}{2}(\mathbf{s} \cdot \nabla)^2(\mathbf{u}^{(n)}(\mathbf{R}_n)) - \ldots\right). \tag{27}$$

On integration,

$$\mathbf{V}^{(n+1)} = \mathbf{u}^{(n)}(\mathbf{R}_n) + \frac{1}{2}\langle (\mathbf{s} \cdot \nabla)^2(\mathbf{u}^{(n)}(\mathbf{R}_n))\rangle + \mathcal{O}(s^4), \tag{28}$$

the average being over chain internal configurations.

The corresponding general equation for the chain rotational velocity follows by analogy with eqs. 18 and 19, and a Taylor expansion, namely

$$\int d\mathbf{s} f(\mathbf{s})g(\mathbf{s})\mathbf{s} \times (\mathbf{V}^{(n+1)} + \mathbf{\Omega}^{(n+1)} \times \mathbf{s}_j + \dot{\mathbf{w}})$$

$$= \int d\mathbf{s} f(\mathbf{s})g(\mathbf{s})\mathbf{s} \times \left(\mathbf{u}^{(n)}(\mathbf{R}_n) + \mathbf{s} \cdot \nabla(\mathbf{u}^{(n)}(\mathbf{R}_n)) + \frac{1}{2}(\mathbf{s} \cdot \nabla)^2(\mathbf{u}^{(n)}(\mathbf{R}_n)) + \dots \right). \tag{29}$$

The integrals reduce to

$$\frac{2F_oS^2}{3}\mathbf{\Omega}^{(n+1)} = \int d\mathbf{s} f(\mathbf{s})g(\mathbf{s})\mathbf{s} \times [(\mathbf{s} \cdot \nabla)\mathbf{u}^{(n)}]. \tag{30}$$

A specific expression for $\mathbf{u}^{(n)}$ may be simplified by applying $\mathbf{s} \cdot \nabla[x] = s_x$, $\mathbf{s} \cdot \nabla[\mathbf{r}] = \mathbf{s}$, $\mathbf{s} \cdot \nabla[\hat{\mathbf{r}}] = \mathbf{s} \cdot [\mathbf{I} - \hat{\mathbf{r}}\hat{\mathbf{r}}]/r$, and $\mathbf{s} \cdot \nabla[1/r^n] = -n\mathbf{s} \cdot \mathbf{r}/r^{n+2}$.

Applying the above to $\mathbf{u}^{(1)}$, one finds

$$\mathbf{V}^{(2)} = \frac{F_o\alpha S^2}{8\pi\eta_o R_1^2}\frac{X_1 Y_1}{R_1^2}\hat{\mathbf{R}}_1 \tag{31}$$

for the translational velocity and

$$\mathbf{\Omega}^{(2)} = \frac{1}{2}\frac{F_o\alpha S^2}{8\pi\eta_o R_1^3}\left[\left(\frac{X_1^2 - Y_1^2}{R_1^2}\right)\hat{\mathbf{k}} + \frac{Y_1 Z_1}{R_1^2}\hat{\mathbf{j}} - \frac{X_1 Z_1}{R_1^2}\hat{\mathbf{i}}\right] \tag{32}$$

for the rotational velocity.

The flow scattered from chain $n+1$ follows from eq. 3, namely

$$\mathbf{u}^{(n+1)}(\mathbf{r}) = \int d\mathbf{s} f(\mathbf{s})g(\mathbf{s})[\mathbf{T}(\mathbf{r}) - \mathbf{s} \cdot \nabla\mathbf{T}(\mathbf{r}) + \mathcal{O}(s^2)]$$

$$\bullet [(\mathbf{V}^{(n+1)} + \mathbf{\Omega}^{(n+1)} \times \mathbf{s} + \dot{\mathbf{w}} - \mathbf{u}^{(n)}(\mathbf{R}_n) - \mathbf{s} \cdot \nabla(\mathbf{u}^{(n)}(\mathbf{R}_n)) - \dots]. \tag{33}$$

Eliminating terms odd in $\mathbf{s}$ and noting eq. 28, a general form for the induced flow is

$$\mathbf{u}^{(n)}(\mathbf{r}) = \int d\mathbf{s} f(\mathbf{s})g(\mathbf{s})(-\mathbf{s} \cdot \nabla_n\mathbf{T}) \cdot [\mathbf{\Omega}^{(n)} \times \mathbf{s} - \mathbf{s} \cdot \nabla_n\mathbf{u}^{(n)}]. \tag{34}$$

Here ∇_n denotes the derivatives with respect to $\mathbf{R}_n$, recalling $\mathbf{u}^{(n)} \equiv \mathbf{u}^{(n)}(\mathbf{R}_1, \mathbf{R}_2, \dots \mathbf{R}_n)$.

To compute $\mathbf{u}^{(2)}$, averages $\langle \mathbf{s}\, \mathbf{a} \cdot [\mathbf{b} \times \mathbf{s}]\rangle = F_o\mathbf{a} \times \mathbf{b}S^3/3$ and $\langle \mathbf{q} \cdot [(\mathbf{s} \cdot \mathbf{a})(\mathbf{b} \times \mathbf{s})]\rangle = F_o\mathbf{q} \cdot (\mathbf{b} \times \mathbf{a})S^2/3$ are applied. A long but direct calculation gives

$$\mathbf{u}^{(2)}(\mathbf{R}_1, \mathbf{R}_2) = +\alpha\left(\frac{F_oS^2}{8\pi\eta_o}\right)^2\frac{\hat{\mathbf{R}}_2}{R_1^3 R_2^2}\left[\frac{X_1 Y_2 + Y_1 X_2}{R_1 R_2}(\hat{\mathbf{R}}_1 \cdot \hat{\mathbf{R}}_2) + \frac{X_1 Y_1}{R_1^2}[1 - 5(\hat{\mathbf{R}}_1 \cdot \hat{\mathbf{R}}_2)^2]\right] \tag{35}$$

for the solvent flow double scattered by chains 1 and 2.

From eq. 28, the third chain in the scattering series has translation velocity

$$\mathbf{V}^{(3)} = \mathbf{u}^{(2)} + \mathcal{O}(s^2). \tag{36}$$

The rotational velocity of the third chain follows from eq. 30 and $\mathbf{u}^{(2)}$, namely

$$\mathbf{\Omega}^{(3)} = \frac{\alpha}{2}\left(\frac{F_oS^2}{8\pi\eta_o}\right)^2\frac{1}{R_1^3 R_2^3}\left[(\hat{\mathbf{R}}_1 \cdot \hat{\mathbf{R}}_2)\frac{(Y_1 Y_2 - X_1 X_2)\hat{\mathbf{k}} - Y_1 Z_2\hat{\mathbf{j}} + X_1 Z_2\hat{\mathbf{i}}}{R_1 R_2}\right.$$

$$\left. + (\hat{\mathbf{R}}_1 \times \hat{\mathbf{R}}_2)\left(\frac{X_1 Y_2 + Y_1 X_2}{R_1 R_2} - \frac{10 X_1 Y_1}{R_1^2}(\hat{\mathbf{R}}_1 \cdot \hat{\mathbf{R}}_2)\right)\right] \tag{37}$$

Further application of eq. 34 to $\mathbf{u}^{(2)}$ and $\mathbf{\Omega}^{(3)}$, followed by integration on the methods used above to obtain $\mathbf{u}^{(2)}$, gives the flow field scattered by the third chain as

$$\mathbf{u}^{(3)} = \frac{\alpha}{3}\left(\frac{F_oS^2}{8\pi\eta_o}\right)^3\frac{1}{R_1^3 R_2^3 R_3^2}\left[\frac{\hat{\mathbf{R}}_1 \cdot \hat{\mathbf{R}}_2}{R_1 R_2 R_3}\left((Y_1 Y_2 - X_1 X_2)(X_3\hat{\mathbf{j}} - Y_3\hat{\mathbf{i}}) + X_1 Z_2(Y_3\hat{\mathbf{k}} - Z_3\hat{\mathbf{j}})\right)\right.$$

$$-Y_1Z_2(Z_3\hat{\mathbf{i}} - X_3\hat{\mathbf{k}})\Big) + 3\hat{\mathbf{R}}_3\left(\frac{Y_1X_2 + X_1Y_2}{R_1R_2} - \frac{10X_1Y_1\hat{\mathbf{R}}_1\cdot\hat{\mathbf{R}}_2}{R_1^2}\right)\left(-\hat{\mathbf{R}}_3\cdot\hat{\mathbf{R}}_2\hat{\mathbf{R}}_3\cdot\hat{\mathbf{R}}_1 + (\hat{\mathbf{R}}_3\cdot\hat{\mathbf{R}}_2)^2\hat{\mathbf{R}}_1\cdot\hat{\mathbf{R}}_2\right)$$

$$-\hat{\mathbf{R}}_3\left(4\hat{\mathbf{R}}_1\cdot\hat{\mathbf{R}}_2\frac{Y_1X_2 + X_1Y_2}{R_1R_2} + \frac{3X_1Y_1[1 - 5(\hat{\mathbf{R}}_1\cdot\hat{\mathbf{R}}_2)^2]}{R_1^2}\right)\left(\mathbf{I} - 3(\hat{\mathbf{R}}_2\cdot\hat{\mathbf{R}}_3)^2\right)$$

$$+\frac{\hat{\mathbf{R}}_1\cdot\hat{\mathbf{R}}_2}{3R_1}\left(\hat{\mathbf{i}}Y_1\hat{\mathbf{R}}_2\cdot\hat{\mathbf{R}}_3 + \hat{\mathbf{j}}X_1\hat{\mathbf{R}}_2\cdot\hat{\mathbf{R}}_3\right.$$

$$+ \hat{\mathbf{R}}_3\left(Y_1\hat{\mathbf{i}}\cdot\hat{\mathbf{R}}_2 - 3Y_1\hat{\mathbf{i}}\cdot\hat{\mathbf{R}}_3\hat{\mathbf{R}}_3\cdot\hat{\mathbf{R}}_2 + X_1\hat{\mathbf{j}}\cdot\hat{\mathbf{R}}_2 - 3X_1\hat{\mathbf{j}}\cdot\hat{\mathbf{R}}_3\hat{\mathbf{R}}_3\cdot\hat{\mathbf{R}}_2\right) - \hat{\mathbf{R}}_2\frac{Y_1X_3 + X_1Y_3}{R_3}\Big)\Bigg] \tag{38}$$

In the iterative process leading to $\mathbf{u}^{(3)}$, each scattering event inserts an additional factor F_oS^2/η_o, the F_o arising from the $\int d\mathbf{s}g(\mathbf{s})f(\mathbf{s})$, the S^2 from the Taylor series expansion, and the η_o from the Oseen tensor.

Because the Oseen tensor describes the flow of an incompressible fluid, for the induced flows one should find $\nabla\cdot\mathbf{u}^{(n)} = 0$. Explicit calculation confirms this expectation for $\mathbf{u}^{(1)}$, $\mathbf{u}^{(2)}$, and $\mathbf{u}^{(3)}$.

III.   PSEUDOVIRIAL EXPANSION FOR THE VISCOSITY

In this section, the viscosity increment due to interchain hydrodynamic interactions is obtained by calculating the excess dissipation arising from the motion of the chains with respect to the solvent. For a system subject to a simple shear $\partial V_y/\partial x$, the dissipated power is

$$\frac{dP}{dV} = \eta\left(\frac{\partial V_y}{\partial x}\right)^2. \tag{39}$$

If we use the usual concentration expansion for the viscosity

$$\eta = \eta_o(1 + [\eta]c + \ldots), \tag{40}$$

for low concentrations

$$\delta\eta \equiv \eta - \eta_o = \eta_o[\eta]c. \tag{41}$$

Eq. 41 links the viscosity increment of dilute chains to the intrinsic viscosity $[\eta]$.

The power dissipated by moving chains in a flow field is

$$P = \left\langle\sum_{j=1}^{N_c}\sum_{i=1}^{N} f_{ij}(\mathbf{v}_{ij} - \mathbf{u}_{ij})^2\right\rangle, \tag{42}$$

the sum proceeding over all N_c chains and N beads of each chain. The ensemble average passes over all chain configurations and positions. Here f_{ij} is the drag coefficient of bead i of chain j while $\mathbf{v}_{ij}$ and $\mathbf{u}_{ij}$ are the bead velocity and the unperturbed solvent velocity at that bead. Eq. 42 describes dilute or non-dilute solutions of hydrodynamically interacting chains.

First note the known dilute-solution result. For dilute identical chains in a simple shear, the dissipated power reduces using eqs. 6, 13, 14, 17, and 21 to

$$P_1 = \langle N_c\sum_{i=1}^{N} f_i(\mathbf{V}^{(1)} + \frac{\alpha}{2}\hat{\mathbf{k}}\times\mathbf{s}_i + \dot{\mathbf{w}}_i - \mathbf{u}^{(0)}(\mathbf{R}_1) - \alpha s_x\hat{\mathbf{j}})^2\rangle. \tag{43}$$

$\mathbf{V}^{(1)}$ and $\mathbf{u}^{(0)}(\mathbf{R}_1)$ cancel. Internal chain modes are independent of a weak small-k shear, so the $\dot{\mathbf{w}}_i$ do not contribute to P_1. Changing variables from $\sum_{i=1}^{N} f_i$ to $\int d\mathbf{s}f(\mathbf{s})g(\mathbf{s})$, applying the identity $(\hat{\mathbf{k}}\times\mathbf{s})\cdot(\hat{\mathbf{k}}\times\mathbf{s}) = s_x^2 + s_y^2$, and averaging $\langle\cdots\rangle$ over chain configurations and positions as described above,

$$P_1 = N_c\frac{F_oS^2}{6}\alpha^2. \tag{44}$$

An average over chain position arises because the velocity shear α depends on chain position. Here the $k \to 0$ limit can be taken before or after the ensemble average.

How is the above calculation extended to non-dilute solutions? Section III described the field scattered from a specific first chain to a specific second chain and so forth. The underlying hydrodynamic equations are linear, so the solvent flow acting on a given bead includes the original imposed flow and also all single-, double-,... scattered flows (cf. eq. 5). Correspondingly, the center-of-mass velocity and rotation rate $\mathbf{V}$ and $\mathbf{\Omega}$ of a chain are the sums of all center-of-mass velocities and rotation rates induced by all the scattered flows.

Notation that systematically represents all scattering events is now required. In some cases chain locations are more useful than displacement vectors. For the flow created at $\mathbf{r}$ by single scattering from a bead at $\mathbf{a}_2$

$$\mathbf{u}^{(1)}(\mathbf{R}_1) \equiv \mathbf{u}^{(1)}(\mathbf{a}_2, \mathbf{r}). \tag{45}$$

Similarly, the double-scattered flow at $\mathbf{r}$ due to beads 2 and 3 is $\mathbf{u}^{(2)}(\mathbf{a}_2, \mathbf{a}_3, \mathbf{r})$ and so forth.

The total single- scattered flow field at $\mathbf{r}$ due to all chains except one (chosen arbitrarily to be chain 1) is

$$\mathbf{u}^{(1T)}(\mathbf{r}) = \sum_{j=2}^{N_c} \mathbf{u}^{(1)}(\mathbf{a}_j, \mathbf{r}). \tag{46}$$

For double-scattered flows,

$$\mathbf{u}^{(2T)}(\mathbf{r}) = \sum_{j=1; k=2; j \neq k}^{N_c} \mathbf{u}^{(2)}(\mathbf{a}_j, \mathbf{a}_k, \mathbf{r}). \tag{47}$$

If chain 1 is at $\mathbf{r}$, so $\mathbf{r} = \mathbf{a}_1$, the $\mathbf{u}^{(1)}(\mathbf{a}_j, \mathbf{a}_1)$, $\mathbf{u}^{(2)}(\mathbf{a}_j, \mathbf{a}_k, \mathbf{a}_1)$,... induce chain motions $\mathbf{V}^{(1)}(\mathbf{a}_j, \mathbf{a}_1)$, $\mathbf{\Omega}^{(2)}(\mathbf{a}_j, \mathbf{a}_k, \mathbf{a}_1)$, ... in accord with eqs. 28 and 30. The zeroth-scattering-order velocities $\mathbf{V}^{(1)} \equiv \mathbf{V}^{(1T)}$ and $\mathbf{\Omega}^{(1)} \equiv \mathbf{\Omega}^{(1T)}$ arise from the initial shear field. Higher-scattering-order components of the chain velocities are due to scattering by all combinations of other particles, so

$$\mathbf{V}^{(2T)}(\mathbf{a}_1) = \sum_{j=2}^{N_c} \mathbf{V}^{(2)}(\mathbf{a}_j, \mathbf{a}_1) \tag{48}$$

and correspondingly

$$\mathbf{\Omega}^{(3T)}(\mathbf{a}_1) = \sum_{j,k=2; j \neq k}^{N_c} \mathbf{\Omega}^{(3)}(\mathbf{a}_j, \mathbf{a}_k, \mathbf{a}_1). \tag{49}$$

In these sums, neighboring arguments of a $\mathbf{u}^{(n)}$, $\mathbf{V}^{(n)}$ or $\mathbf{\Omega}^{(n)}$ must be distinct.

The total translational and rotational velocities of chain 1 are

$$\mathbf{V} = \sum_{n=1}^{\infty} \mathbf{V}^{(nT)} \tag{50}$$

and

$$\mathbf{\Omega} = \sum_{n=1}^{\infty} \mathbf{\Omega}^{(nT)}. \tag{51}$$

The Debye form for the power dissipated by a representative chain is

$$P = \sum_{i=1}^{N} f_i (\mathbf{V}^{(1T)} + \mathbf{\Omega}^{(1T)} \times \mathbf{s}_i + \mathbf{V}^{(2T)} + \mathbf{\Omega}^{(2T)} \times \mathbf{s}_i + \ldots - \mathbf{u}^{(0)}(\mathbf{r}_i) - \mathbf{u}^{(1T)}(\mathbf{r}_i) - \ldots)^2. \tag{52}$$

To simplify this expression, the fluid velocity at bead i is expanded around chain 1's center-of-mass location,

$$\mathbf{u}^{(1T)}(\mathbf{r}_i) = \mathbf{u}^{(1T)}(\mathbf{a}_1) + \mathbf{s}_i \cdot \nabla(\mathbf{u}^{(1T)}(\mathbf{a}_1)) + \ldots. \tag{53}$$

Limiting expansions to terms of lowest order in $\mathbf{s}$, eq. 28 shows $\mathbf{V}^{(n+1T)}$ and $\mathbf{u}^{(nT)}$ cancel term-by-term for all n, so

$$P = \sum_{i=1}^{N} f_i [\mathbf{\Omega}^{(1T)} \times \mathbf{s}_i + \mathbf{\Omega}^{(2T)} \times \mathbf{s}_i + \ldots - \mathbf{s}_i \cdot \nabla \mathbf{u}^{(0)}(\mathbf{a}_1) - \mathbf{s}_i \cdot \nabla \mathbf{u}^{(1T)}(\mathbf{a}_1) - \ldots]^2. \tag{54}$$

Expanding the square yields three classes of terms. Averaging over chain configurations,

$$\langle (\mathbf{s} \cdot \nabla) \mathbf{u}^{(n)} \cdot (\mathbf{s} \cdot \nabla) \mathbf{u}^{(m)} \rangle \equiv \left\langle \sum_{i,j,m=(x,y,z)} \mathbf{s}_i \frac{\partial \mathbf{u}_m^{(a)}}{\partial x_i} \cdot \mathbf{s}_j \frac{\partial \mathbf{u}_m^{(b)}}{\partial x_j} \right\rangle = \left\langle \frac{S^2}{3} \sum_{i,m=(x,y,z)} \frac{\partial \mathbf{u}_m^{(a)}}{\partial x_i} \frac{\partial \mathbf{u}_m^{(b)}}{\partial x_i} \right\rangle. \tag{55}$$

On the other hand,

$$\langle (\mathbf{\Omega}^{(a)} \times \mathbf{s}) \cdot (\mathbf{\Omega}^{(b)} \times \mathbf{s}) \rangle = \frac{2}{3} S^2 \mathbf{\Omega}^{(a)} \cdot \mathbf{\Omega}^{(b)}. \tag{56}$$

The cross terms are

$$\langle \mathbf{\Omega}^{(a)} \times \mathbf{s} \cdot (\mathbf{s} \cdot \nabla) \mathbf{u}^{(b)} \rangle = \langle \mathbf{\Omega}^{(a)} \cdot \mathbf{s} \times (\mathbf{s} \cdot \nabla \mathbf{u}^{(b)}) \rangle, \tag{57}$$

while from eq. 30

$$\langle \mathbf{s} \times (\mathbf{s} \cdot \nabla) \mathbf{u}^{(b)} \rangle = \frac{2 F_o S^2}{3} \mathbf{\Omega}^{(b+1)}. \tag{58}$$

From the above

$$P = \sum_{a,b=0}^{\infty} P_{a,b} \tag{59}$$

with

$$P_{a,b} = \left\langle \frac{F_o S^2}{3} \left[\sum_{i,j=1}^{3} \left[\mathbf{u}_{i,j}^{(aT)} \mathbf{u}_{i,j}^{(bT)} \right] - 2 \mathbf{\Omega}^{(a+1T)} \cdot \mathbf{\Omega}^{(b+1T)} \right] \right\rangle. \tag{60}$$

The Einstein derivative notation $\mathbf{u}_{l,j}^{(aT)} \equiv (\partial \mathbf{u}^{(aT)} \cdot \hat{\mathbf{l}}/\partial x_j)$ (for $j, l = 1, 2, 3$) is in use. The average is over all particle positions; $a \neq b$ is allowed. For example, a particle rotating at $\mathbf{\Omega}^{(2)}$ is moving not only with respect to the original $\mathbf{u}^{(1)}$ but also with respect to the imposed shear $\mathbf{u}^{(0)}$. These relative motions both contribute to the dissipated power.

IV. THE TOTAL SHEAR

The above treated fluid flows and power dissipation in a polymer solution subject to an imposed shear field $du_y^{(0)}/dx = u_0 \sin(kx)$. Beyond the imposed shear, flows were obtained from a multiple scattering series $\mathbf{u}^{(1)}$, $\mathbf{u}^{(2)}$,... Each scattered flow contributes to the total fluid flow $\mathbf{u}^{(T)}$ and to the relevant shear, $du_y^{(T)}/dx$.

Physically, only the total fluid flow and its derivatives are experimentally accessible. One measures the time required for a fluid to pass through a pipe, the force required to move a plate at a certain speed, or the like. These measurements determine the total fluid velocity, including all scattered flows. In the above dissipations were instead obtained in terms of the imposed $\mathbf{u}^{(0)}$. The imposed shear is only part of the total flow, and is inaccessible to physical observation. To compare model and experiment, the imposed shear must be replaced by the total shear. This replacement is somewhat analogous to the replacement that arises in calculating the dielectric constant, in which one must treat simultaneously the induced dipoles and the total electric field including material contributions, as discussed by Peterson and Fixman[11].

The shear fields due to single and double scattering are

$$\frac{du_y^{(1)}(\mathbf{R_1})}{dx} = \frac{F_o S^2}{8 \pi \eta R_1^3} \left(\frac{Y_1^2}{R_1^2} - \frac{5 X_1^2 Y_1^2}{R_1^4} \right) u_0 k \sin(k(X - x_1)) \tag{61}$$

and

$$\frac{du_y^{(2)}(\mathbf{R_2})}{dx} = \left(\frac{F_o^2 S^4}{(8\pi\eta)^2 R_1^3 R_2^3}\right) \frac{y_2}{R_2} \left(-5\frac{x_1 y_2 + x_2 y_1}{R_1 R_2}\frac{x_2}{R_2}\hat{\mathbf{R}}_1 \cdot \hat{\mathbf{R}}_2 - 3\frac{x_1 y_1 x_2}{R_1^2 R_2}(1 - 5(\hat{\mathbf{R}}_1 \cdot \hat{\mathbf{R}}_2)^2)\right.$$

$$\left. -10\frac{x_1^2 y_1 \hat{\mathbf{R}}_1 \cdot \hat{\mathbf{R}}_2}{R_1^3} + \frac{y_1}{R_1}\hat{\mathbf{R}}_1 \cdot \hat{\mathbf{R}}_2 + \frac{x_1}{R_1}\frac{x_1 y_2 + x_2 y_1}{R_1 R_2} + \frac{10 x_1 y_1 x_2 (\hat{\mathbf{R}}_1 \cdot \hat{\mathbf{R}}_2)^2}{R_1^2 R_2}\right) u_o k \sin(k(X - x_1 - x_2)) \quad (62)$$

The shear field resulting all from single- and double-scattering events is obtained by ensemble averaging over all particles in the solution. Performing the final integrals with Mathematica,

$$\left\langle \frac{du_y^{(1)}}{dx}\right\rangle = \frac{16\pi}{15}\frac{F_0 S^2}{8\pi\eta}cu_0 k \sin(kx), \quad (63)$$

for the single-scattered shear, c being the number density N/V of polymer molecules. For the double-scattered shear,

$$\left\langle \frac{du_y^{(2)}}{dx}\right\rangle = -\frac{16\pi^2}{75}\frac{F_0^2 S^4}{\eta^2}c^2 u_o k \sin(kx) \quad (64)$$

Integrals of r^{-3} over all space are potentially delicate. The use of a spatially-oscillatory imposed shear field, later taken to the long-wavelength limit, leads to convergent integrals for $\langle\frac{du_y^{(1)}}{dx}\rangle$ and $\langle\frac{du_y^{(2)}}{dx}\rangle$, at least when R_1 and R_2 are integrated over ranges $[a, b]$, the limits $b \to \infty$ and $a \to 0$ then being taken. From eqs 14, 63, and 64,

$$\left\langle \frac{du_y^{(T)}(x)}{dx}\right\rangle = -u_o k \sin(kx)\left[1 - \frac{2}{15}\frac{F_0 S^2}{\eta}c + \frac{16\pi^2}{75}\frac{F_0^2 S^4}{\eta^2}c^2 + \mathcal{O}(c^3)\right] \quad (65)$$

the average being over all chain positions.

V. LINEAR AND QUADRATIC TERMS

The simplest term in the series expansion for the power is $P_{0,0}$. In a direct evaluation of $P_{0,0}$ from eq. 60, only the x-component of $\mathbf{u}_{.j}^{(0)}$ is non- zero, while $\mathbf{\Omega}^{(1)}$ is found above.

$$P_{0,0} = \left\langle N_c \frac{F_o S^2}{3}\left[(u_o k \cos(ka_{1x})\hat{\mathbf{j}})^2 - 2(\frac{1}{2}u_o k \cos(ka_{1x})\hat{\mathbf{k}})^2\right]\right\rangle. \quad (66)$$

where now $\langle\cdots\rangle$ denotes a conventional ensemble average over particle center-of-mass locations. Here the ensemble average and the $k \to 0$ limit can be taken in either order. Including contributions by all N_c particles,

$$P_{0,0} = \frac{N_c F_o S^2}{6}\frac{(u_o k)^2}{2}. \quad (67)$$

The series expansion for P is infinite, requiring truncation or resummation for evaluation. This paper advances via truncation. There are two inequivalent truncation variables. One could sort terms by the number of scattering events that they include. One could also sort terms by the number of distinct particles that they include.

Uniquely, the lowest order truncation of the series includes all terms involving zero or fewer scattering events and simultaneously includes all terms involving only one or fewer polymer chains. All higher-order truncations are incomplete: either they omit terms involving a given number of scattering events, or alternatively they omit terms involving a given number of particles. Higher-order $P_{a,b}$ include terms that only involve a few chains, because flow fields can be scattered back and forth between two chains an arbitrary number of times. However, comparison of $\mathbf{u}^{(1)}$, $\mathbf{u}^{(2)}$, and $\mathbf{u}^{(3)}$ shows that each additional back-scattering event reduces interaction range by an additional $1/r^3$. This paper retains only the longest-range part of the interaction tensors, in which a $\mathbf{u}^{(n)}$ couples $n + 1$ distinct chains.

The structure of the expansion, independent of numerical details, constrains the quantitative form of $\eta(c)$. In particular, the series of chains contributing to an $\mathbf{\Omega}^{(a)}(\mathbf{a}_2, \ldots, \mathbf{a}_a, \mathbf{a}_1)$ are only constrained not to be pairwise adjacent:

$\mathbf{a}_3$ and $\mathbf{a}_4$ may not refer to the same particle, but $\mathbf{a}_3$ and $\mathbf{a}_5$ may. Terms in which, e.g., $\mathbf{a}_3$ and $\mathbf{a}_5$ refer to the same chain effectively involve a shorter range r^{-6} interaction between chains 3 and 4 than do terms in which $\mathbf{a}_3$ and $\mathbf{a}_5$ refer to two distinct chains. By analogy with the equilibrium theory of electrolyte solutions, in which leading terms come from ring diagrams, the leading terms of $P_{a,b}$ will arise from scattering series $\mathbf{a}_2, \ldots, \mathbf{a}_a, \mathbf{a}_1$ in which all particles are distinct.

In $\mathbf{u}_{i,j}^{(aT)}\mathbf{u}_{i,j}^{(bT)}$ and in $\mathbf{\Omega}^{(a+1T)} \cdot \mathbf{\Omega}^{(b+1T)}$, the chains in the a and b terms may be the same or may differ wholly or in part. When ensemble averages are taken, one obtains for each independent $\mathbf{a}_j$ a factor N_c corresponding to the number of polymer chains that j could have represented. Each such chain also corresponds to a scattering event, giving a factor $F_o S^2/\eta_o$. $P_{0,0}$ as evaluated above is also proportional to $(c[\eta])^1$. Each independent $\mathbf{a}_j$ in a higher-order term gives a factor $N_c F_o S^2/\eta_o \sim c[\eta]$, so the leading terms of the $P_{a,b}$ and hence P itself are predicted by the model here to be power series in $c[\eta]$. The model thus agrees with the phenomenological observation that $[\eta]$ is a good reducing variable for c.

At long range, the hydrodynamic interaction tensors describing the $\mathbf{\Omega}^{(n)}$ and $\mathbf{u}^{(n)}$ depend on interparticle spacings as r^{-3}. An ensemble average over an r^{-3} interaction gives a logarithmic divergence to P, mirroring the need to treat system boundaries, as seen in the hydrodynamic calculation[20] of the colloid mutual diffusion coefficient. As seen below, in this calculation divergences were suppressed by taking a sinusoidal imposed flow $\sim u_o \cos(kx)$ and then the long-wavelength $k \to 0$ limit.

The hydrodynamic interaction tensors obtained above also have short range divergences. Physical considerations imply there is an effective short range cut-off, because $u^{(n)}$ and $\Omega^{(n)}$ should be finite at small s. This cut-off was treated by Peterson and Fixman[11], who proposed that two overlapped chains have zero relative velocity and move as a rigid dumbbell.

The above formalism is now used to compute the $\mathcal{O}(c^2)$ contributions to η. The $P_{a,b}$ with longest-range two-chain terms have $a + b = 1$ or $a = b = 1$. For $a + b = 1$, there are two identical terms

$$P_{1,0} = P_{0,1} = \int d\mathbf{a}_1 d\mathbf{a}_2 \ldots d\mathbf{a}_{N_c} \exp(-\beta(W_{N_c} - A_{N_c}) \left[\sum_{p \neq q = 1}^{N_c} \frac{F_o S^2}{3} (-2\mathbf{\Omega}^{(1)}(\mathbf{a}_p) \cdot \mathbf{\Omega}^{(2)}(\mathbf{a}_q, \mathbf{a}_p) \right.$$

$$\left. + \sum_{i,j=1}^{3} \left[\mathbf{u}_{i,j}^{(0)}(\mathbf{a}_p)\mathbf{u}_{i,j}^{(1)}(\mathbf{a}_q, \mathbf{a}_p) \right] \right)\right] \tag{68}$$

An ensemble average over internal chain coordinates gave the S^2. The ensemble average over the chain center-of-mass coordinates $\mathbf{a}_i$ is for once written explicitly. Here $\beta = (k_B T)^{-1}$, k_B is Boltzmann's constant, T is the absolute temperature, W_{N_c} is the potential energy, A_{N_c} is the Helmholtz free energy, and p and q label chains.

All terms of the sum over p and q are identical save for label. The ensemble average is

$$P_{1,0} = \frac{F_o S^2 N_c (N_c - 1)}{3} \int d\mathbf{a}_1 d\mathbf{a}_2 \left[\left(\sum_{i,j=1}^{3} \left[\mathbf{u}_{i,j}^{(0)}(\mathbf{a}_1)\mathbf{u}_{i,j}^{(1)}(\mathbf{a}_2, \mathbf{a}_1) \right] \right.\right.$$

$$\left.\left. -2\mathbf{\Omega}^{(1)}(\mathbf{a}_1) \cdot \mathbf{\Omega}^{(2)}(\mathbf{a}_2, \mathbf{a}_1) \right) \int d\mathbf{a}_3 \ldots d\mathbf{a}_M \exp(-\beta(W_M - A_M)) \right] \tag{69}$$

In this equation, the non-zero derivative of $\mathbf{u}^{(0)}$ is

$$\mathbf{u}_{,x}^{(0)} = -u_o k \sin(ka_{1x})\hat{\mathbf{j}} \tag{70}$$

while the corresponding derivative of $\mathbf{u}^{(1)}$ is

$$u_{,x}^{(1)} = u_o k \sin(k(a_{1x} - X_1)) \frac{F_o S^2}{8\pi\eta_o} \left[\left(\frac{Y_1}{R_1^4} - \frac{5X_1^2 Y_1}{R_1^6} \right) \hat{\mathbf{R}}_1 + \frac{X_1 Y_1}{R_1^5}\hat{\mathbf{i}} \right]. \tag{71}$$

a_{1x} is the final particle in the scattering sequence and $\mathbf{R}_1$ points from the penultimate to the ultimate particle of the scattering sequence.

The corresponding angular velocities are given by eqs. 21 and 32. In each equation α is the shear at the first particle of the scattering series, so the two shears are respectively proportional to $-u_o k \sin(ka_{1x})\hat{\mathbf{j}}$ and $u_o k \sin(k(a_{1x} - X_1))\hat{\mathbf{j}}$.

The identity $\sin(ka_{1x})\sin(k(a_{1x} - X_1)) = (-\cos(2ka_{1x} - kX_1) + \cos(kX_1))/2$ is applied. The ensemble average only depends on $\mathbf{a}_1$ through $\cos(2ka_{1x} - kX_1)$, which vanishes in the ensemble average.

Applying the definition

$$\frac{g^{(2)}(\mathbf{r})}{V^2} = \frac{\int d\mathbf{a}_3 \ldots d\mathbf{a}_M \exp(-\beta W(\mathbf{r}, \mathbf{a}_3, \ldots \mathbf{a}_M))}{\int d\mathbf{a}_1 \ldots d\mathbf{a}_{N_c} \exp(-\beta W(\mathbf{r}, \mathbf{a}_3, \ldots \mathbf{a}_{N_c}))} \tag{72}$$

of the radial distribution function, with system volume V and $\mathbf{r} = \mathbf{a}_2 - \mathbf{a}_1$,

$$P_{1,0} = -\left(\frac{u_o^2 k^2}{2}\right)\left(\frac{N_c(N_c - 1)(F_o S^2)^2}{24\pi\eta_o V}\right)\int d\mathbf{R}\, g^{(2)}(R)\frac{\cos(kX)}{R^3}\left[\frac{X^2 + Y^2}{R^2} - \frac{10X^2Y^2}{R^4}\right]. \tag{73}$$

A lower cut-off is allowed in the radial integral but is not needed for $P_{1,0}$. If the factor $\cos(kx)$ were absent, the radial integral would diverge at large R; the angular integral would vanish; the $\int d\mathbf{R}$ would be improper. The $\int d\mathbf{R}$ and the $k \to 0$ limit cannot be interchanged. The proper long-wavelength limit is obtained by first integrating over $\mathbf{R}$ and then taking the limit $k \to 0$. Equivalently, if the calculation had begun with a purely linear shear rather than an oscillatory velocity field, $P_{1,0}$ would be divergent, as observed a half-century ago by Saito[9].

Setting the $\mathbf{k}$ vector to be parallel to the X axis, a useful identity[17] is

$$\cos(\mathbf{k} \cdot \mathbf{R}) = 4\pi\sum_{l=0}^{\infty}\frac{i^l + (-i)^l}{2}j_l(kr)(4\pi(2l+1))^{1/2}Y_{l0}(\gamma) \tag{74}$$

with j_l denoting a spherical bessel function, and the spherical harmonic Y_{l0} being a function of the angle between $\mathbf{k}$ and $\mathbf{R}$.

Transforming to spherical coordinates, recourse to Mathematica gives

$$P_{1,0} = -\eta_o\frac{N_c^2 - N_c}{V}\frac{48\pi}{5}\left(\frac{F_o S^2}{6\eta_o}\right)^2\left(\frac{u_o^2 k^2}{2}\right). \tag{75}$$

The sign of this term is surprising. One ordinarily expects friction to increase dissipation. However, in the intrinsically positive form $(a - b)^2$ the term $-2ab$ can be negative. Physically, eq. 75 has its sign because the flow field $\mathbf{u}^{(1)}$ causes chain 2 to rotate, thereby reducing the velocity difference between chain 2 and $\mathbf{u}^{(0)}$, thereby reducing the dissipation.

Consider now $P_{1,1}$. Beginning with eq. 60, writing the total rotational velocity and solvent flow of particle 1 as sums of the rotations and flows caused by each of the other particles, and recalling that all N_c particles contribute to $P_{1,1}$ in the same way that particle 1 contributes,

$$P_{1,1} = \left\langle \frac{N_c F_o S^2}{3}\left(-2\sum_{p,q=2}^{N_c}\mathbf{\Omega}^{(2)}(\mathbf{a}_p, \mathbf{a}_1) \cdot \mathbf{\Omega}^{(2)}(\mathbf{a}_q, \mathbf{a}_1) + \sum_{p,q=2}^{N_c}\sum_{i,j=1}^{3}\left[\mathbf{u}_{j,i}^{(1)}(\mathbf{a}_p, \mathbf{a}_1)\mathbf{u}_{j,i}^{(1)}(\mathbf{a}_q, \mathbf{a}_1)\right]\right)\right\rangle \tag{76}$$

The sums in eq. 76 are usefully separated into self ($p = q$) and distinct ($p \neq q$) terms, the latter yielding only terms cuic in concentration. To $\mathcal{O}(c^2)$

$$P_{1,1} = \frac{N_c(N_c - 1)F_o S^2}{3V}\left(\int d\mathbf{a}_1 d\mathbf{a}_2\, g^{(2)}(\mathbf{a}_1, \mathbf{a}_2)\mathbf{\Omega}^{(2)}(\mathbf{a}_2, \mathbf{a}_1) \cdot \mathbf{\Omega}^{(2)}(\mathbf{a}_2, \mathbf{a}_1) + \sum_{i,j=1}^{3}\left[\mathbf{u}_{j,i}^{(1)}(\mathbf{a}_2, \mathbf{a}_1)(\mathbf{u}_{j,i}^{(1)}(\mathbf{a}_2, \mathbf{a}_1)\right]\right) + \ldots \tag{77}$$

This term is sufficiently strongly convergent at large R that the integrals and the $k \to 0$ limit may be exchanged, giving

$$P_{1,1,s} = \frac{c^2 V F_o S^2}{6}\alpha^2\left(\frac{F_o S^2}{8\pi\eta_o}\right)^2$$

$$\times \int_V d\mathbf{R}\frac{1}{R^6}\left[\frac{6X^2Y^2 - X^4 - Y^4 + Z^4}{R^4} + \frac{2X^2 + 2Y^2 - Z^2}{R^2}\right]g^{(2)}(R) \tag{78}$$

$P_{1,1,s}$ only converges if there is a short-range cutoff a on the radial integral. It is physically appropriate to insert such a cutoff. Eqs. 26 and 32 are the long-range part of series expansions. Physically, if chains 1 and 2 are perfectly

overlapped chain 2 will simply move with chain 1 and its entrained solvent; the contribution to $P_{1,1,s}$ will be small. Short-range terms that eliminate divergences in $\mathbf{u}$ and $\mathbf{\Omega}$ are here empirically represented by a cut-off distance a. ($P_{1,0}$ converges without this cutoff. Inserting the cutoff into $P_{1,0}$ has only a small effect on $P_{1,0}$.)

Integrating, one obtains

$$P_{1,1,s} = \left(\frac{F_o S^2}{8\pi\eta}\right)^2 \frac{4\pi F_o S^2}{15a^3} c^2 \frac{(u_o k)^2}{2} \tag{79}$$

Combining eqs 65, 67, 75, and 79,

$$\eta\left(\left\langle\frac{du_y^{(T)}}{dx}\right\rangle\right)^2 = \eta_o\left[1 + \frac{F_o S^2}{6\eta_o}c + \left(-\frac{4\pi F_o^2 S^4}{15\eta_o^2} + \frac{F_o^3 S^6}{240\pi\eta_o^3 a^3}\right)c^2\right]\left[1 - \frac{2}{15}\frac{F_0 S^2}{\eta}c + \frac{16\pi^2}{75}\frac{F_0^2 S^4}{\eta^2}c^2\right]^{-2}\left(\left\langle\frac{du_y^{(T)}(x)}{dx}\right\rangle\right)^2 \tag{80}$$

On expanding series, in terms of eq 1

$$[\eta] = \frac{13 F_o S^2}{30\eta_o} \tag{81}$$

and

$$k_H = \frac{88 - 240\pi - 384\pi^2}{169} + \frac{225[\eta]}{4394\pi a^3} \tag{82}$$

The cutoff radius a is a crude approximation replacing a sound treatment of the hydrodynamics of interpenetrating random coils. If the approximation is reasonable a should be some number moderately smaller than the radius R of a polymer coil.

How large is a? Two approaches to estimating a suggest themselves. From Pearson[18] and Yamakawa[19], k_H is in the range 0.3-0.6. Noting for nondraining spheres $[\eta] = 2.5\bar{v}$ and in appropriate units $\bar{v} = 4\pi R^3/3$, one finds from eq 82 $a = 0.18R$. The estimated a does not depend strongly on the assumed k_H.

Second, in ref. [3] the same hydrodynamic approach was applied to the self-diffusion coefficient D_s, obtaining[3] for $\alpha = dD_s/dc$ at small c

$$\alpha = -\frac{9}{16}\frac{R_{h1}^2}{R_g a_D}\frac{4\pi R_g^3}{3}\frac{N_A}{M}. \tag{83}$$

where here R_g is the radius of gyration, R_h is the hydrodynamic radius, a_D is the cutoff length from self-diffusion, N_A is Avogadro's number, and M is the polymer molecular weight. For[22] 1.27×10^6 Da polystyrene in benzene[22], $R_g \approx 620$Å, $R_h \approx 380$Å, and from a systematic review[23] of the published literature $\alpha \approx -0.6$ with c in g/L at this molecular weight. Combining these findings, $a_D \approx 0.17R_g$, which is not greatly different from the $a \approx 0.18R$ estimated from the known k_H. Determinations of a from two separate types of data after separate calculations (above and [2, 3]) using our model lead to about the same cutoff length.

VI. DISCUSSION

The above gives a systematic path, based on a generalized Kirkwood-Riseman model[1], to calculate the viscosity of a non-dilute polymer solution. Hydrodynamic interactions for polymer molecules in a weak shear field were determined, based on multiple scattering of an imposed weak shear by a series of chains. General forms suitable for iteration, and specific forms for up to three chains were obtained. The relationship between the imposed shear acting on the first chain and the total shear measured experimentally was found. Finally, a general process for using these forms to calculate the viscosity was developed. The general form for $\eta(c)$ is readily extended to higher order in c. Extrapolation to elevated c via a renormalization group is then readily[3, 4] performed.

The process for calculating $\eta(c)$ leads naturally to a power series in $c[\eta]$. The finding that $\eta(c)$ is a natural series in $c[\eta]$ is consistent with the literature. The Martin equation gives

$$\eta - \eta_0 = \eta_0 c[\eta]\exp(k_H c[\eta]). \tag{84}$$

Adler and Freed[24] present a hydrodynamic calculation invoking effective medium arguments that leads to eq. 84, at least for $c[\eta]$ of order unity of less, and for very large polymers "before the onset of entanglements". Simha

and Utracki[25] and Dreval, et al.[26] showed empirically that $c[\eta]$ is a good reducing variable for experimental measurements of $\eta(c)$, sometimes for $c[\eta]$ as large as 15 or 30.

A significant complication in calculating η is that the hydrodynamic interaction tensors depend on distance as r^{-3}, leading to divergences at short and long range. As recounted above, some earlier attempts to obtain $\eta(c)$ from a Kirkwood-Risemann approach gave k_H in terms of improper integrals lacking proper convergence properties. These divergences were here eliminated by using a sinusoidal rather than a linear shear field and by introducing a short-range physical cutoff distance a. The cutoff distances estimated from k_H and separately from $D_s(c)$ are approximately equal, consistent with the belief that this approximation procedure is not inappropriate.

Acknowledgement

[1] J. G. Kirkwood and J. Riseman, Journal of Chemical Physics **16**, 565 (1948).

[2] G. D. J. Phillies, Macromolecules **20**, 558 (1987); G. D. J. Phillies, Macromolecules **21**, 3101 (1988); G. D. J. Phillies and P. C. Kirketelos, Journal of Polymer Science B: Polymer Physics **31**, 1785 (1993).

[3] G. D. J. Phillies, Macromolecules, **31**, 2317 (1998).

[4] A. R. Altenberger and J. S. Dahler, Physical Review E **54**, 6242 (1996); A. R. Altenberger and J. S. Dahler, J. Colloid Interface Science **189**, 379 (1997).

[5] D. V. Shirkov, International Journal of Modern Physics A **3**, 1321 (1988); N. N. Bogoliubov and D. V. Shirkov, "Quantum Fields", Benjamin/Cummings, Reading (1983); D. V. Shirkov, Teoreticheskaya i Matematicheskaya Fizika **60**, 218 (1984).

[6] H. C. Brinkman, *J. Chem. Phys.* **20**, 571 (1952).

[7] J. Riseman and R. Ullman, *J. Chem. Phys.* **19**, 578 (1951).

[8] N. Saito, *J. Phys. Soc. Japan* **5**, 4 (1949).

[9] N. Saito, *J. Phys. Soc. Japan* **7**, 447 (1952).

[10] H. Yamakawa, *J. Chem. Phys.* **34**, 1360 (1960).

[11] J. M. Peterson and M. Fixman, *J. Chem. Phys.* **39**, 2516 (1963).

[12] S. F. Edwards and K. F. Freed, *J. Chem. Phys.* **61**, 1189 (1974).

[13] K. F. Freed and S. F. Edwards, *J. Chem. Phys.* **61**, 3626 (1974).

[14] K. F. Freed and S. F. Edwards, *J. Chem. Phys.* **62**, 4032 (1975).

[15] K. F. Freed and A. Perico, *Macromolecules* **14**, 1290 (1981).

[16] A. R. Altenberger, J. S. Dahler, and M. Tirrell, *Macromolecules* **21**, 464 (1988).

[17] J. D. Jackson, *Classical Electrodynamics*, John Wiley (New York): 1962, p. 567.

[18] D. S. Pearson, *Rubber Chem. Technol.* **60**, 439-496 (1987).

[19] H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper & Rowe, New York: 1971, Ch. 6.

[20] J. M. Carter and G. D. J. Phillies, *J. Phys. Chem.* **89**, 5118 (1985).

[21] G. D. J. Phillies, *Macromolecules* **21**, 3101 (1988)

[22] M. Adam and M. Delsanti, *Macromolecules*, **10**, 1229 (1977).

[23] , G. D. J. Phillies, *in preparation.*

[24] R. S. Adler and K. F. Freed, *J. Chem. Phys.* **72** 4186-4193 (1980).

[25] R. Simha and L. Utracki, *Rheol. Acta*, **12**, 455 (1973).

[26] V. E. Dreval, A. Ya. Malkin, and G. O. Botvinnik, *J. Polym. Sci., Polym. Phys. Ed.* **11**, 1055 (1971).