Macromolecules **1981**, *14*, 1290–1298

(5) Ono, K.; Okano, K. *Jpn. J. Appl. Phys.* **1970**, *9*, 1356.
(6) Evans, G. T. *J. Chem. Phys.* **1979**, *71*, 2263.
(7) Fixman, M.; Evans, G. T. *J. Chem. Phys.* **1978**, *68*, 195. Fixman, M. *Ibid.* **1978**, *69*, 1527, 1538.
(8) Shore, J. E.; Zwanzig, R. *J. Chem. Phys.* **1975**, *63*, 5445.
(9) Barkley, M. D.; Zimm, B. H. *J. Chem. Phys.* **1979**, *70*, 2991.
(10) Allison, S. A.; Schurr, J. M. *Chem. Phys.* **1979**, *41*, 35.
(11) An early attempt to account for damped torsional oscillations was made by Tobolsky and DuPre (Tobolsky, A. V.; DuPre, D. B. *Adv. Polym. Sci.* **1969**, *6*, 103). However, they did not treat angular coordinates explicitly and ascribed the damping to the velocity of a given segment rather than to the *relative* velocity of adjacent segments as done in ref 9 and 10.
(12) Reference 1, p 149.
(13) Reference 1, Chapter 7.
(14) Brink, D. M.; Satchler, G. R. "Angular Momentum"; Oxford University Press: New York, 1968.
(15) Aragon, S.; Pecora, R. *J. Chem. Phys.* **1977**, *66*, 2506.
(16) Pecora, R. *J. Chem. Phys.* **1968**, *48*, 4126.
(17) Pecora, R. *J. Chem. Phys.* **1968**, *49*, 1032.
(18) Skolnick, J.; Helfand, E. *J. Chem. Phys.* **1980**, *72*, 5489.
(19) Kramers, H. A. *Physica (Utrecht)* **1940**, *7*, 284.
(20) Norisuye, T.; Yu, H. *J. Chem. Phys.* **1978**, *68*, 4038.
(21) Lin, Y.-H.; Wang, C. H. *J. Chem. Phys.* **1977**, *66*, 5578.
(22) Abromowitz, M.; Stegun, I. A. *Natl. Bur. Stand. (U.S.) Appl. Math. Ser.* **1964**, *No. 55*.
(23) Whittaker, E. T.; Watson, G. N. "A Course of Modern Analysis"; Cambridge University Press: London, 1973; p 171.

Considerations on the Multiple Scattering Representation of the Concentration Dependence of the Viscoelastic Properties of Polymer Systems

Karl F. Freed*

The James Franck Institute and the Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

Angelo Perico

Centro Studi Chimico-Fisici di Macromolecole Sintetiche e Naturali, Consiglio Nazionale delle Ricerche, 16132 Genova, Italia. Received February 23, 1981

ABSTRACT: The multiple scattering theory for the concentration dependence of the viscoelastic properties of polymer solutions is rederived with a discrete bead-type model for the polymer chains and the familiar Rouse and Zimm matrices. The use of the discrete chain model is helpful to eliminate errors arising from considering the limits of long wavelength, low frequencies, and long (essentially continuous) chains in improper orders or in an approximate fashion. The discrete chain representation enables us to prove the following theorems for *phantom polymer chains*: (i) There is no hydrodynamic screening, i.e., no Darcy's law retarding forces on the polymers, for individual chains at infinite dilution. (ii) Theorem i enables us to convert the multiple scattering theory correlation function for the frequency-dependent intrinsic viscosity identically into the Rouse–Zimm expression within the preaveraging approximation. (iii) The hydrodynamic screening is shown to vanish term by term in the multiple scattering expansion and, hence, to all orders in concentration. From theorem iii and results on the concentration dependence of the viscosity of suspensions of spheres, it becomes clear that the origin of hydrodynamic screening lies in the presence of entanglements and interchain interactions. The mathematical complexity of the description of entanglements leads us to consider only a qualitative phenomenological model of the hydrodynamic screening and the transition it induces from low-concentration Rouse–Zimm-type behavior to high-concentration Rouse-like hydrodynamic properties.

1. Introduction

The Rouse–Zimm theory[1,2] has been widely successful in providing a molecular basis for the understanding of the viscoelastic and frictional properties of individual polymer chains in solution.[3] Despite its enormous utility, the theory is limited to the case of infinite dilution (one polymer molecule), very low frequencies ($\lesssim 10^4$–10^6 Hz), and zero shear rate (a stationary fluid). A treatment of the higher frequencies requires a molecular understanding of the phenomena which have been classified under the phenomenological heading of internal viscosity, while a description at nonzero shear rates necessitates a fully nonlinear theory.

We have provided a comprehensive theory of the concentration dependence of the viscoelastic properties of polymer solutions based upon a multiple scattering formulation.[4-11] In this representation the fluid velocity field is represented as a superposition of all possible processes in which the incident fluid velocity field has its flow patterns disturbed, or scattered, by no polymer chains, by one chain, by two chains, etc., with all possible sequences of scattering by many chains. The theory has been implemented in dilute and in concentrated solutions. In the latter case an effective medium theory[6-10] is utilized to provide a physically simple self-consistent formulation of the concentration-dependent hydrodynamics. The infinite-dilution limit is found to agree with the Rouse–Zimm predictions of the frequency-dependent intrinsic viscosity $[\eta(\omega)]$, although a detailed proof has not yet been given to demonstrate that the multiple scattering representation correlation function expression for $[\eta(\omega)]$ is indeed equivalent to the Rouse–Zimm theory. Here we show, in fact, within the popular preaveraging approximation the complete equivalence of the two theories at infinite dilution.

The multiple scattering theory of Freed and Edwards is, however, also applicable for nonzero polymer concentrations. The theory has shown the importance of "hydrodynamic screening" in producing a transition from a Rouse–Zimm-like viscosity function, depending on $cM^{1/2}$ (in Θ solvents), where c is the polymer mass concentration and M is the molecular weight, at lower concentrations to a cM-dependent viscosity for high concentrations but nonmacroscopically entangled solutions. This

0024-9297/81/2214-1290$01.25/0

"hydrodynamic screening" is a mathematical description of the emergence of a Darcy's law retarding force[13] on the fluid motion.

In the proof of the equivalence of the Rouse–Zimm and the infinite-dilution-limit multiple scattering representations of $[\eta(\omega)]$ it is shown that hydrodynamic screening vanishes identically within a single *phantom* polymer chain.[13] Furthermore, it is proven that the hydrodynamic screening is likewise absent to all orders in the multiple scattering expansion and to all orders in concentration, *for phantom chains* with unaveraged, anisotropic hydrodynamic interactions. This result emerges because the *phantom* polymer molecules are free to drift with the fluid with the polymer-averaged perturbed local fluid velocity. This free drifting at high concentrations undoubtedly requires that the phantom chains pass through each other. Of course, actual polymers are not phantom chains, so the emergence of hydrodynamic screening, if present, must somehow be associated with those forces that distinguish real polymer molecules from phantom chains, namely, entanglements.

The molecular basis for the emergence of hydrodynamic screening can be extracted from the theory of Freed and Muthukumar concerning the concentration dependence of the hydrodynamics of suspensions of spheres.[10,14,15] Phantom Brownian spheres can drift with the local perturbed fluid velocity, so hydrodynamic screening is absent.[15] Hard-sphere (or other) interactions at low sphere concentrations cannot alter this physical characteristic. At the other extreme, however, when the spheres are held fixed, hydrodynamic screening is obviously present because the fixed spheres do provide a net retarding force to the fluid's motion.[14] Now, as the concentration of, say, hard spheres is increased, the interparticle forces ultimately result in the formation of a glass (provided the ultimate crystallization is somehow inhibited). The glass corresponds to a system of fixed spheres (apart from a small number of degrees of freedom) with hydrodynamic screening. Thus, the onset of hydrodynamic screening must appear at some physically accessible concentration of spheres.

The situation with polymer chains is similar,[10] except for the fact that the polymers are spread out over a much larger volume. Thus, at rather low concentrations long polymer chains interpenetrate. This results in the emergence of gel modes in the semidilute region due to the interpenetration and entanglement of the polymer molecules. Here the entanglements impede the unhindered ability of a single chain to perfectly follow the perturbed fluid flow, so hydrodynamic screening is present. The theory in the concentrated regime follows similar to that previously given by Freed and Edwards, and the screening in the dilute regime is considerably reduced. The original calculations are marred, however, by errors of factors of 2 that arise because of subtle complications due to reversal of the orders in which the long-wavelength hydrodynamic, the zero-frequency, and the long-chain limits are taken.[9,16] Hence, a more systemmatic analysis is provided here, utilizing the more popular discrete chain model[3] where the details of the limiting procedures can safely be controlled.

In section 2 we briefly provide the discrete chain representation of the basic multiple scattering theory. Section 3 gives the proof that hydrodynamic screening vanishes within a single phantom polymer chain. This theorem then enables a demonstration of the equivalence of the Rouse–Zimm and multiple scattering expressions for $[\eta(\omega)]$ within the preaveraging approximation. (We believe that the latter approximation is not required and that the unaveraged theories should be equivalent.) The proof of the absence of hydrodynamic screening for *phantom* chains to all orders in the multiple scattering theory is presented in section 4, while section 5 contains a qualitative phenomenological description of the emergence of hydrodynamic screening for real polymer molecules.

2. Multiple Scattering Theory

A. Equations of Motion. We consider a system with N polymer molecules in a fluid of volume V, with the thermodynamic limit of $N \to \infty$, $V \to \infty$, $N/V \to$ constant being invoked at the end of the calculation. Each individual chain α contains n monomer units at the spatial positions $\mathbf{R}_{i\alpha}(t)$, $i = 1, ..., n$, where t is the time. For simplicity, the chain is taken to be described in terms of Rouse "bead–spring" entropic forces appropriate to idealized Θ conditions for phantom polymer chains. The equation of motion for the polymer, ignoring its inertia, is given by

$$\kappa \sum_m A_{im} \mathbf{R}_{m\alpha}(t) = -\sigma_{i\alpha}(t) \tag{2.1}$$

with κ the "force constant", $\kappa = 3k_\mathrm{B}T/l^2$, l the Kuhn length, $k_\mathrm{B}T$ the absolute temperature in energy units, A_{im} the Rouse matrix[1,3]

$$A_{im} = \begin{cases} 2\delta_{im} - \delta_{i,m+1} - \delta_{i,m-1} & i, m \neq 1 \text{ or } n \\ \delta_{im} - \delta_{i,m+1} & i = 1 \\ \delta_{im} - \delta_{i,m-1} & i = n \end{cases} \tag{2.2}$$

and $\sigma_{i\alpha}(t)$ the force exerted by the ith monomer on chain α on the fluid. The random forces, driving the Brownian motion of the polymers, are contained in $\sigma_{i\alpha}(t)$ in addition to all frictional forces. A phenomenological treatment for non-Θ conditions may be invoked[8,9] by employing scaled concentration-dependent values of κ and A_{ij}, but these models require further investigation.

In the limit of zero shear rate the dynamics of the fluid is governed by the linearized Navier–Stokes equation subject to the forces $\sigma_{i\alpha}(t)$ supplied by the polymer. If $\mathbf{v}(\mathbf{r},t)$ is the fluid velocity at $\mathbf{r}$ and t, the total force density exerted by the polymers on the fluid at $\mathbf{r}$ and t is $\sum_{i,\alpha}\delta[\mathbf{r} - \mathbf{R}_{i\alpha}(t)]\sigma_{i\alpha}(t)$, so the fluid equation is

$$\left(\rho_0 \frac{\partial}{\partial t} - \eta_0 \nabla^2\right)\mathbf{v}(\mathbf{r},t) + \vec{\nabla}P(\mathbf{r},t) = \mathbf{F}^*(\mathbf{r},t) + \sum_{i,\alpha}\delta[\mathbf{r} - \mathbf{R}_{i\alpha}(t)]\sigma_{i\alpha}(t) \tag{2.3}$$

where ρ_0 and η_0 are the pure fluid's density and viscosity, respectively. $P(\mathbf{r},t)$ is the hydrostatic pressure that is determined from the incompressibility constraint

$$\vec{\nabla}\cdot\mathbf{v}(\mathbf{r},t) = 0 \tag{2.4}$$

and $\mathbf{F}^*(\mathbf{r},t)$ is the random thermal force fluctuations which are required such for $t \to \infty$ the pure fluid alone would come to thermal equilibrium. The thermal equilibrium condition implies that $\mathbf{F}^*(\mathbf{r},t)$ vanish on average and have the correlation function

$$\langle \mathbf{F}_\lambda^*(\mathbf{r},t)\mathbf{F}_\mu^*(\mathbf{r}',t')\rangle = 2\delta_{\mu\lambda}k_\mathrm{B}T\delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \qquad \mu, \lambda = x, y, z \tag{2.5}$$

Within the simple Rouse chain model it is the presence of the random forces $\mathbf{F}^*$ which drive the chain Brownian motion through the hydrodynamic boundary conditions relating the polymer and fluid velocities. The simplest no-slip boundary conditions are

$$\mathbf{v}(\mathbf{R}_{i\alpha}(t),t) = \dot{\mathbf{R}}_{i\alpha} \equiv \frac{\partial}{\partial t}\mathbf{R}_{i\alpha}(t) \qquad \text{all } i, \alpha \tag{2.6}$$

These boundary conditions enable the unique determination of the friction forces $\{\sigma_{i\alpha}(t)\}$ in (2.1) and (2.3). Note that $\mathbf{v}(\mathbf{r},t)$ in (2.3), (2.4), and (2.6) represents the *perturbed* fluid velocity at $\mathbf{r}$ and t in the presence of the polymers. As demonstrated below (see also ref 6 and 14), this hydrodynamic boundary condition leads to the usual Oseen-type hydrodynamic interactions between monomers and to the usual friction forces, proportional to the difference between the "bead" velocity $\mathbf{R}_{i\alpha}(t)$ and the fluid velocity *in the absence of the polymer,* which is invoked in the Kirkwood–Riseman and Rouse–Zimm theories. In conformity with these theories, the mathematics is enormously simplified by utilizing a point friction model for the monomers. The theory could be formulated in terms of, say, spherical monomer units. Then if the leading multipole expansion were employed, the results would be as given below, provided the individual bead friction coefficient is inserted [cf. discussion following after (2.15)].

For low enough frequencies the dynamics of the pure fluid alone, the $\rho_0(\partial/\partial t)\mathbf{v}(\mathbf{r},t)$ term in (2.3), can be neglected, and (2.3) reduces to[17]

$$-\eta_0\nabla^2\mathbf{v}(\mathbf{r},t) + \vec{\nabla}P(\mathbf{r},t) = \mathbf{F}^*(\mathbf{r},t) + \sum_{i,\alpha}\delta[\mathbf{r} - \mathbf{R}_{i\alpha}(t)]\sigma_{i\alpha}(t) \quad (2.7)$$

Note that (2.7) still depends on time because the polymers are undergoing dynamical motion.

B. Macroscopic Fluid Equations. Ultimately it is necessary to perform a configurational average over the distribution function for the polymers at some initial time. Since the zero shear rate limit is under consideration, the averaging involves the equilibrium polymer distribution. Note that the solution of (2.7) implies that $\mathbf{v}(\mathbf{r},t)$ depends on all of the $\{\mathbf{R}_{i\alpha}(t)\}$, so we may perform the configurational average of (2.7) to yield

$$-\eta_0\nabla^2\mathbf{u}(\mathbf{r},t) + \vec{\nabla}P(\mathbf{r},t) = \mathbf{F}^*(\mathbf{r},t) + \langle\sum_{i,\alpha}\delta[\mathbf{r} - \mathbf{R}_{i\alpha}(t)]\sigma_{i\alpha}(t)\rangle \quad (2.8)$$

where the angular brackets denote averaging over the polymer equilibrium distribution, $\mathbf{u}(\mathbf{r},t) \equiv \langle\mathbf{v}(\mathbf{r},t)\rangle$, and $\langle P\rangle$ is written simply as P. The last term on the right in (2.8) is the total friction force density at $\mathbf{r}$ exerted by the polymers on the fluid at time t. In the linear viscoelastic region this friction force density is proportional to $\mathbf{u}(\mathbf{r},t)$, but the proportionality is, in general, nonlocal in space and time. This may be expressed as

$$\langle\sum_{i,\alpha}\delta[\mathbf{r} - \mathbf{R}_{i\alpha}(t)]\sigma_{i\alpha}(t)\rangle = \int \mathrm{d}\mathbf{r}'\int_{t_0}^{t}\mathrm{d}t'\,\Sigma(\mathbf{r} - \mathbf{r}'; t - t')\cdot\mathbf{u}(\mathbf{r}',t') + O(\mathbf{u}^2) \quad (2.9)$$

where Σ is the fluid friction coefficient density tensor which has been termed the "self-energy" by mathematical analogy with many-body theory.

As noted above the $O(\mathbf{u}^2)$ terms are neglected here. The right-hand side may also be represented as a gradient expansion

$$\langle\sum_{i,\alpha}\delta[\mathbf{r} - \mathbf{R}_{i\alpha}(t)]\sigma_{i\alpha}(t)\rangle = \int_{t_0}^{t}[\boldsymbol{D}(t - t') + \delta\eta(t - t')\nabla^2 + \boldsymbol{b}(t - t')\nabla^4 + \ldots]\cdot\mathbf{u}(\mathbf{r},t')\,\mathrm{d}t' \quad (2.9a)$$

The existence of a spatially homogeneous term $\boldsymbol{D}$ implies the presence of a Darcy's law net retarding force on the fluid and hydrodynamic screening. Substituting (2.9a) into (2.8) makes it clear that $\delta\eta(t - t')$ is the contribution to the average solution dynamical viscosity which is due to the polymers, while $\boldsymbol{b}(t - t')$ is the dynamical Burnett coefficient, etc. Hence, given Σ we may determine all of the polymer contributions to the hydrodynamic coefficients $\boldsymbol{D}$, $\delta\eta$, $\boldsymbol{b}$, ... It is generally conventional to express the dynamical quantities in terms of frequencies, and this is accomplished by use of Fourier transforms

$$\delta\eta(\omega) = \lim_{\epsilon\to 0^+}\int_0^\infty \mathrm{d}\tau\,\exp(-i\omega\tau - \epsilon\tau)\delta\eta(\tau) \quad (2.10a)$$

$$\Sigma(\mathbf{r} - \mathbf{r}', \omega) = \lim_{\epsilon\to 0^+}\int_0^\infty \mathrm{d}\tau\,\exp(-i\omega\tau - \epsilon\tau)\Sigma(\mathbf{r} - \mathbf{r}', \tau) \quad (2.10b)$$

The integrals in (2.10) range only over $\tau = t - t' \geq 0$ because the system cannot respond before an applied force. Hence, the response functions must be proportional to the step function $\theta(t - t')$. This *causality* condition on Σ implies that its time Fourier transform must be an analytic function of ω in the lower half complex ω plane to ensure that the inverse Fourier transform, giving $\Sigma(\mathbf{r} - \mathbf{r}'; t - t')$ from $\Sigma(\mathbf{r} - \mathbf{r}', \omega)$, be proportional to $\theta(t - t')$. Hence, real frequencies must be approached from the lower half plane, resulting in the ϵ-limiting procedure in (2.10). This limit makes the Fourier integrals be well-defined, and it is important in view of the fact that $\delta\eta(\tau)$ and $\Sigma(\mathbf{r} - \mathbf{r}', \tau)$ are often expressed in terms of correlation functions. The $\epsilon \to 0^+$ limit then enables us to freely interchange the orders of the τ and other integrals which otherwise would not be permissible.[18]

Use of (2.9) to order $\mathbf{u}$ or (2.9a) in (2.8), along with the incompressibility constraint $\vec{\nabla}\cdot\mathbf{u}(\mathbf{r},t) = 0$, produces a simple hydrodynamic problem with the force density $\mathbf{F}^* + \Sigma\cdot\mathbf{u}$ which is readily solved formally in terms of the Oseen tensor

$$\boldsymbol{G}(\mathbf{r} - \mathbf{r}') = (8\pi\eta_0|\mathbf{r} - \mathbf{r}'|)^{-1}[\boldsymbol{I} + (\mathbf{r} - \mathbf{r}')(\mathbf{r} - \mathbf{r}')|\mathbf{r} - \mathbf{r}'|^{-2}] \quad (2.11)$$

If the imposed flow field in the absence of the polymers is $\mathbf{v}_0(\mathbf{r},t)$, the "solution" of (2.8) with (2.9) is simply

$$\mathbf{u}(\mathbf{r},t) = \mathbf{v}_0^*(\mathbf{r},t) + \int \mathrm{d}\mathbf{r}'\,\mathrm{d}\mathbf{r}''\int_{t_0}^{t}\mathrm{d}t'\,\boldsymbol{G}(\mathbf{r} - \mathbf{r}')\cdot\Sigma(\mathbf{r}' - \mathbf{r}''; t - t')\cdot\mathbf{u}(\mathbf{r}'',t') \quad (2.12)$$

where $\mathbf{v}_0^* \equiv \mathbf{v}_0 + \mathbf{v}^*$ and $\mathbf{v}^*(\mathbf{r},t) = \int\mathrm{d}\mathbf{r}'\,\boldsymbol{G}(\mathbf{r} - \mathbf{r}')\cdot\mathbf{F}^*(\mathbf{r},t)$ are the random velocity fluctuations in the fluid. Equation 2.12 may be iterated indefinitely to produce

$$\mathbf{u}(\mathbf{r},t) = \mathbf{v}_0^*(\mathbf{r},t) + \int\mathrm{d}\mathbf{r}'\,\mathrm{d}\mathbf{r}''\int_{t_0}^{t}\mathrm{d}t'\,\boldsymbol{G}(\mathbf{r} - \mathbf{r}')\cdot\Sigma(\mathbf{r}' - \mathbf{r}''; t - t')\cdot\mathbf{v}_0^*(\mathbf{r}'',t') + \int\boldsymbol{G}\cdot\Sigma\cdot\boldsymbol{G}\cdot\Sigma\cdot\mathbf{v}_0^* + \int\boldsymbol{G}\cdot\Sigma\cdot\boldsymbol{G}\cdot\Sigma\cdot\boldsymbol{G}\cdot\Sigma\cdot\mathbf{v}_0^* + \ldots \quad (2.13)$$

where the higher order terms in the series are written in symbolic form with dummy variables and integrations implicit. Equation 2.13 may be averaged over the random velocity fluctuations. Since $\langle\mathbf{v}^*\rangle = 0$, the averaging eliminates these terms.

The general method for treating the concentration dependence of the hydrodynamics of polymer solutions is to attempt to solve the basic microscopic equations of motion (2.1), (2.7), and (2.6) as an expansion in $\boldsymbol{G}$. After performing the configurational average over polymer conformations, one can, by comparison of this result with (2.13), determine Σ and then the hydrodynamic quantities from (2.9a). The related effective medium theory[7,10] takes the hydrodynamic disturbances to be propagated through the average polymer solution as described by the effective concentration-dependent hydrodynamic interactions $\hat{\boldsymbol{G}}(\mathbf{r}$

$- \mathbf{r}'; c)$ rather than the Oseen tensor $\boldsymbol{G}(\mathbf{r} - \mathbf{r}')$. The expansion procedure is more involved, but the basic techniques are related.

C. Solution of the Equations of Motion. If the $\mathbf{R}_{i\alpha}(t)$ and $\sigma_{i\alpha}(t)$ were known, then (2.7) could trivially be integrated to give

$$\mathbf{v}(\mathbf{r},t) = \mathbf{v}_0^*(\mathbf{r},t) + \sum_{i,\alpha} \boldsymbol{G}[\mathbf{r} - \mathbf{R}_{i\alpha}(t)] \cdot \sigma_{i\alpha}(t) \qquad (2.14)$$

Note that $\mathbf{v}(\mathbf{r},t)$ in (2.14) is the velocity at the point $\mathbf{r}$ and time t in the fluid. But because of the point monomer model, the no-slip boundary condition (2.6) implies that (2.14) is equally valid as the bead velocity for the points $\mathbf{r}$ equaling $\mathbf{R}_{i\alpha}$.

Applying the hydrodynamic boundary condition (2.6) for $j\beta$ to (2.14) yields

$$\dot{\mathbf{R}}_{j\beta}(t) = \mathbf{v}(\mathbf{R}_{j\beta}(t),t) = \mathbf{v}_0^*(\mathbf{R}_{j\beta}(t),t) + \sum_{i,\alpha} \boldsymbol{G}[\mathbf{R}_{j\beta}(t) - \mathbf{R}_{i\alpha}(t)] \cdot \sigma_{i\alpha}(t) \qquad (2.15)$$

Because the monomers are taken as point sources of friction, the self-term $\boldsymbol{G}[\mathbf{R}_{j\beta}(t) - \mathbf{R}_{i\alpha}(t)]$ for $j\beta = i\alpha$ is undefined. This difficulty would be rectified by treating the monomers as spheres of nonzero radius. Then it is readily shown that the self-term $\boldsymbol{G}$ is just $\zeta^{-1}\mathbf{1}$, where ζ is the bead friction coefficient. In the following, this is assumed to be implicit in the definition of $\boldsymbol{G}$. For a single bead (2.15) yields the friction force equal to $\zeta[\dot{\mathbf{R}} - \mathbf{v}_0^*(\mathbf{R})]$, while for a single chain (2.15) may be rearranged[6] to the standard Kirkwood–Riseman force equation (cf. eq 31.7 of Yamakawa[3]). These results follow from the use of the boundary conditions (2.6).[14]

Multiplying the polymer equation (2.11) by the quantity $\sum_{i,\alpha} \boldsymbol{G}[\mathbf{R}_{j\beta}(t) - \mathbf{R}_{i\alpha}(t)] \cdot$ produces

$$\sum_{i,m,\alpha} \boldsymbol{G}[\mathbf{R}_{j\beta}(t) - \mathbf{R}_{i\alpha}(t)] \kappa A_{im} \cdot \mathbf{R}_{m\alpha}(t) = -\sum_{i,\alpha} \boldsymbol{G}[\mathbf{R}_{j\beta}(t) - \mathbf{R}_{i\alpha}(t)] \cdot \sigma_{i\alpha}(t) \qquad (2.16)$$

The term in $\boldsymbol{G} \cdot \sigma$ may be eliminated between (2.15) and (2.16), leaving

$$\dot{\mathbf{R}}_{j\beta}(t) + \sum_{i,m} \boldsymbol{G}[\mathbf{R}_{j\beta}(t) - \mathbf{R}_{i\beta}(t)] \kappa A_{im} \cdot \mathbf{R}_{m\beta}(t) = \mathbf{v}_0^*(\mathbf{R}_{j\beta}(t),t) - \sum_{\substack{\alpha \neq \beta \\ i,m}} \boldsymbol{G}[\mathbf{R}_{j\beta}(t) - \mathbf{R}_{i\alpha}(t)] \kappa A_{im} \cdot \mathbf{R}_{m\alpha}(t) \qquad (2.17)$$

where we have separated the sum over all α into $\alpha = \beta$ and $\alpha \neq \beta$. The first three terms in (2.17) provide the Langevin equation for a Rouse chain with hydrodynamic interactions $\boldsymbol{G}$ in a fluid with imposed velocity $\mathbf{v}_0$ and random velocity fluctuations $\mathbf{v}^*$. The latter have the spectrum

$$\langle \mathbf{v}_\lambda^*(\mathbf{R}_{j\beta}(t),t) \mathbf{v}_\mu^*(\mathbf{R}_{i\beta}(t'),t') \rangle = 2k_{\mathrm{B}}TG_{\lambda\mu}[\mathbf{R}_{j\beta}(t) - \mathbf{R}_{i\beta}(t)] \delta(t - t') \qquad (2.5a)$$

$$\lambda, \mu = x, y, z$$

as deduced from (2.5). The last term on the right in (2.17) arises from the hydrodynamic disturbances due to the remaining chains in solution.

We assume that single-polymer problems may be solved (at least approximately). A formal solution of (2.17) is written as

$$\mathbf{R}_{j\beta}(t) = \sum_m \int_{t_0}^{t} \mathrm{d}t' \, \boldsymbol{g}_{jm}(t,t') \cdot \{\mathbf{v}_0^*(\mathbf{R}_{m\beta}(t'),t') - \sum_{\alpha \neq \beta,i,p} \boldsymbol{G}[\mathbf{R}_{m\beta}(t') - \mathbf{R}_{i\alpha}(t')] \kappa A_{ip} \cdot \mathbf{R}_{p\alpha}(t')\} \qquad (2.18)$$

where $\boldsymbol{g}_{jm}(t,t')$ is the fundamental solution for the single polymer

$$\left\{ \frac{\partial}{\partial t} \mathbf{1} \delta_{jp} + \sum_i \boldsymbol{G}[\mathbf{R}_{j\beta}(t) - \mathbf{R}_{i\beta}(t)] \kappa A_{ip} \right\} \cdot \boldsymbol{g}_{pm}(t,t') = \delta_{jm} \mathbf{1} \delta(t - t') \qquad (2.19)$$

Note that $\boldsymbol{g}_{jm}(t,t')$ is a function of the instantaneous monomer positions $\{\mathbf{R}_{j\beta}(t)\}$, so (2.19) cannot be solved exactly. In the preaveraging approximation[2,3] $\boldsymbol{G}$ is replaced by its average $\langle \boldsymbol{G} \rangle$, enabling (2.19) to be solved. The $\langle \boldsymbol{G} \rangle$ is proportional to the H matrix of Rouse–Zimm[2,3,19] theory by

$$\langle \boldsymbol{G} \rangle = H \mathbf{1} \zeta^{-1} \qquad (2.11a)$$

Expansions in $\boldsymbol{G} - \langle \boldsymbol{G} \rangle$ can then be generated to obtain $\boldsymbol{g}_{pm}(t,t')$.[6]

Equation 2.18 can be iterated indefinitely in the last $\boldsymbol{G}A \cdot \mathbf{R}$ terms on the right to yield

$$\mathbf{R}_{j\beta}(t) = \sum_m \int_{t_0}^{t} \mathrm{d}t' \, \boldsymbol{g}_{jm}(t,t') \cdot \left\{ \mathbf{v}_0^*(\mathbf{R}_{m\beta}(t'),t') - \sum_{\alpha \neq \beta,i,p} \int_{t_0}^{t} \mathrm{d}t'' \, \boldsymbol{G}[\mathbf{R}_{m\beta}(t') - \mathbf{R}_{i\alpha}(t')] \times \kappa A_{ip} \cdot \boldsymbol{g}_{pq}(t',t'') \cdot \mathbf{v}_0^*(\mathbf{R}_{q\alpha}(t''),t'') \right\} + \sum_{\alpha \neq \beta} \sum_{\gamma \neq \beta} \int \boldsymbol{g} \cdot \boldsymbol{G}[\mathbf{R}_\beta - \mathbf{R}_\alpha] \kappa A \cdot \boldsymbol{g} \cdot \boldsymbol{G}[\mathbf{R}_\alpha - \mathbf{R}_\gamma] \kappa A \cdot \boldsymbol{g} \mathbf{v}_0^* + \ldots \qquad (2.20)$$

where the last term is written in symbolic form with indices, integrations, and summations implicit. The formal "solution" for $\{\mathbf{R}_{m\alpha}(t)\}$ from (2.20) can be substituted into the left-hand side of (2.1) to provide a formal solution for $\sigma_{i\alpha}(t)$ as the multiple scattering series

$$\sigma_{i\alpha}(t) = -\kappa A \boldsymbol{g} \cdot \mathbf{v}_0^* + \sum_{\beta \neq \alpha} \kappa A \boldsymbol{g} \cdot \boldsymbol{G}(\mathbf{R}_\alpha - \mathbf{R}_\beta) \cdot \kappa A \boldsymbol{g} \mathbf{v}_0^* - \sum_{\beta \neq \alpha} \sum_{\gamma \neq \beta} \kappa A \boldsymbol{g} \cdot \boldsymbol{G}(\mathbf{R}_\alpha - \mathbf{R}_\beta) \kappa A \cdot \boldsymbol{g} \cdot \boldsymbol{G}(\mathbf{R}_\beta - \mathbf{R}_\gamma) \kappa A \cdot \boldsymbol{g} \mathbf{v}_0^* + \ldots \qquad (2.21)$$

When inserted into (2.14), the configurational average over polymer conformations may be taken. The average over the random velocity fluctuations can be performed likewise, and the $\langle \mathbf{v}^* \rangle$ terms then vanish.

In order to convert the multiple scattering species for $\mathbf{u}$ into the form of (2.13), the argument of $\boldsymbol{G}$ and $\mathbf{v}_0$ must be rewritten in terms of positions in the fluid. This is accomplished by use of identities

$$\boldsymbol{G}[\mathbf{R}_{i\alpha}(t) - \mathbf{R}_{j\beta}(t')] \equiv \int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{r}' \, \delta[\mathbf{r} - \mathbf{R}_{i\alpha}(t)] \boldsymbol{G}(\mathbf{r} - \mathbf{r}') \delta[\mathbf{r} - \mathbf{R}_{j\beta}(t')] \qquad (2.22a)$$

$$\mathbf{v}_0(\mathbf{R}_{j\beta}(t),t) \equiv \int \mathrm{d}\mathbf{r} \, \delta[\mathbf{r} - \mathbf{R}_{j\beta}(t)] \mathbf{v}_0(\mathbf{r},t) \qquad (2.22b)$$

Substitution of (2.21) and (2.22) into (2.14) yields a formal solution for the velocity field $\mathbf{v}(\mathbf{r},t)$ at any point in the fluid. By (2.6) this also gives the bead velocity $\mathbf{R}_{i\alpha}(t)$ if $\mathbf{r}$ coincides with any $\mathbf{R}_{i\alpha}(t)$. We defined $\mathbf{u}(\mathbf{r},t) = \langle \mathbf{v}(\mathbf{r},t) \rangle$ as the configurationally averaged velocity field at point $(\mathbf{r},t)$ in the *polymer solution*. The $\langle \; \rangle$ denotes an average over an equilibrium polymer distribution at some initial time in the distant past. Further writing $\bar{\mathbf{u}}(\mathbf{r},t)$ as the average of $\mathbf{u}(\mathbf{r},t)$ over the random velocity fluctuations in the fluid, after considerable algebra, we find the average solution velocity field (linear in $\mathbf{v}_0$) can be written as

$$\bar{\mathbf{u}}(\mathbf{r},t) = \mathbf{v}_0(\mathbf{r},t) - \sum_\alpha \int \mathrm{d}\mathbf{r}' \, \mathrm{d}\mathbf{r}'' \, \boldsymbol{G}(\mathbf{r} - \mathbf{r}') \cdot \langle \boldsymbol{T}_\alpha(\mathbf{r}',\mathbf{r}'',t,t'|\{\mathbf{R}_{i\alpha}(t)\}) \rangle \cdot \mathbf{v}_0(\mathbf{r}'',t') \, \mathrm{d}t' + \langle \sum_\alpha \sum_{\beta \neq \alpha} \boldsymbol{G} \cdot \boldsymbol{T}_\alpha \cdot \boldsymbol{G} \cdot \boldsymbol{T}_\beta \cdot \mathbf{v}_0 \rangle - \langle \sum_\alpha \sum_{\beta \neq \alpha} \sum_{\gamma \neq \beta} \boldsymbol{G} \cdot \boldsymbol{T}_\alpha \cdot \boldsymbol{G} \cdot \boldsymbol{T}_\beta \cdot \boldsymbol{G} \cdot \boldsymbol{T}_\gamma \cdot \mathbf{v}_0 \rangle + \ldots \qquad (2.23)$$

where $\bar{\mathbf{u}}$ indicates that the average over random velocity fluctuations has been taken and

$$\boldsymbol{T}_\alpha(\mathbf{r},\mathbf{r}',t,t'|\{\mathbf{R}_{i\alpha}(t)\}) = \\ + \sum_{i,j,m} \delta[\mathbf{r} - \mathbf{R}_{i\alpha}(t)]\kappa A_{ij}\boldsymbol{g}_{jm}(t,t'|\{\mathbf{R}_{p\alpha}(t)\})\delta[\mathbf{r}' - \mathbf{R}_{m\alpha}(t')] \tag{2.24}$$

describes the dynamical scattering of the fluid by a single polymer chain. Note that in the last term in (2.23) we may have $\gamma = \alpha$ or $\gamma = \alpha$, so this term has portions of second and third order in polymer concentration c, respectively. Comparing (2.23) with (2.13) (for $\bar{\mathbf{u}}$) enables Σ to be determined as

$$\Sigma(\mathbf{r} - \mathbf{r}'; t - t') = -\sum_\alpha \langle \boldsymbol{T}_\alpha(\mathbf{r},\mathbf{r}',t,t'|\{\mathbf{R}_{i\alpha}(t)\})\rangle - \\ \sum_\alpha \sum_{\beta\neq\alpha} \{\langle \boldsymbol{T}_\alpha\cdot\boldsymbol{G}\cdot\boldsymbol{T}_\beta\cdot\boldsymbol{G}\cdot\boldsymbol{T}_\alpha\rangle - \langle \boldsymbol{T}_\alpha\cdot\boldsymbol{G}\cdot\boldsymbol{T}_\beta\cdot\boldsymbol{G}\cdot\boldsymbol{T}_\alpha\cdot\boldsymbol{G}\cdot\boldsymbol{T}_\beta\rangle + ...\} - \\ \sum_\alpha \sum_{\beta\neq\alpha} \sum_{\gamma\neq\beta,\alpha} \{\langle \boldsymbol{T}_\alpha\cdot\boldsymbol{G}\cdot\boldsymbol{T}_\beta\cdot\boldsymbol{G}\cdot\boldsymbol{T}_\gamma + ...\rangle\} + ... \tag{2.25}$$

where (2.25) is derived under the assumption that the polymers are noninteracting, uncorrelated phantom chains. A more general treatment for interacting particles will be given elsewhere.

In the next section we analyze the properties of $\langle \boldsymbol{T}_\alpha\rangle$ to describe hydrodynamic screening and viscosity for a single chain, the inifinite-dilution limit, while section 4 discusses the homogeneous portion of (2.25) which governs the concentration dependence of hydrodynamic screening for phantom chains.

3. Screening and Viscosity at Infinite Dilution

In the limit of infinite dilution the first term on the right of (2.25) in $\langle \boldsymbol{T}_\alpha\rangle$ gives the leading contribution. The average over all polymer conformations is taken in two stages. First we average over all center-of-mass positions $\mathbf{R}_\alpha^0$ by using

$$\mathbf{R}_{i\alpha} = \mathbf{R}_\alpha^0 + \mathbf{r}_{i\alpha} \tag{3.1}$$

Equation 2.19 implies that $\boldsymbol{g}_{pm}$ depends only on relative internal positions, $\mathbf{r}_{j\beta} - \mathbf{r}_{i\beta}$, so the only terms in (2.24) depending on $\mathbf{R}_\alpha^0$ are the δ functions. The center-of-mass averaging utilizes the distribution $\prod_\alpha[V^{-1}\int \mathrm{d}\mathbf{R}_\alpha^0]$. The integral

$$\int \mathrm{d}\mathbf{R}_\alpha^0\ \delta[\mathbf{r} - \mathbf{R}_\alpha^0 - \mathbf{r}_{i\alpha}(t)]\delta[\mathbf{r}' - \mathbf{R}_\alpha^0 - \mathbf{r}_{m\alpha}(t')] = \\ \delta[\mathbf{r} - \mathbf{r}' - \mathbf{r}_{i\alpha}(t) - \mathbf{r}_{m\alpha}(t')] \tag{3.2}$$

and the fact that all chains contribute equally to $\sum_\alpha\langle \boldsymbol{T}_\alpha\rangle$ imply that (2.25) reduces to

$$\Sigma(\mathbf{r} - \mathbf{r}'; t - t') = -(N/V)\sum_{i,j,m} \langle\delta[\mathbf{r} - \mathbf{r}' - \mathbf{r}_{i\alpha}(t) + \\ \mathbf{r}_{m\alpha}(t')]\kappa A_{ij}\boldsymbol{g}_{jm}(t,t'|\{\mathbf{r}_{p\alpha}(\tau)\})\rangle + O(c^2) \tag{3.3}$$

with the average now only over the internal $\{\mathbf{r}_{i\alpha}\}$ distribution. Note that we have explicitly ignored the difference between $\mathbf{R}_\alpha^0(t)$ and $\mathbf{R}_\alpha^0(t')$ due to center-of-mass Brownian motion. If included,[6,20] this would add a term in $\mathbf{R}_\alpha^0(t') - \mathbf{R}_\alpha^0(t)$ to the argument of the δ function in (3.3). Averaging over the random forces would then produce the additional overall factor of $\exp(-D_0k^2|t - t'|)$ in $\Sigma(\mathbf{k}, t - t')$ below,[20] with D_0 the chain translational diffusion coefficient.

It is convenient to introduce the spatial Fourier transforms of Σ to define

$$\Sigma(\mathbf{k}, t - t') = -(N/V) \times \\ \sum_{i,j,m} \langle\exp\{i\mathbf{k}\cdot[\mathbf{r}_i(t) - \mathbf{r}_m(t')]\}\kappa A_{ij}\boldsymbol{g}_{jm}(t,t'|\{\mathbf{r}_p(\tau)\})\rangle + O(c^2) \tag{3.4}$$

where the $\{\mathbf{r}_i\}$ refer to a single chain at infinite dilution. The spatial Fourier transforms of (2.9) can be compared with (3.4) to show that $\boldsymbol{D}(t - t')$ is equal to $\Sigma(\mathbf{k} = 0, t - t')$, that $\delta\eta(t - t')$ is the negative of the coefficient of $\mathbf{k}^2$ in $\Sigma(\mathbf{k}, t - t')$, $\mathbf{b}(t - t')$ is the coefficient of $\mathbf{k}^4$, etc.

A. Vanishing of Hydrodynamic Screening for Individual Phantom Chains. Consider first the hydrodynamic screening constant $\boldsymbol{D}(t - t')$ given by

$$\boldsymbol{D}(t - t') \equiv \Sigma^{(0)}(\mathbf{k} = 0, t - t') = \\ -(N/V)\sum_{i,j,m} \kappa A_{ij}\langle \boldsymbol{g}_{jm}(t,t'|\{\mathbf{r}_p(\tau)\})\rangle \tag{3.5}$$

The Rouse matrix A_{ij} of (2.2) has the simple property that

$$\sum_i A_{ij} = \sum_j A_{ij} \equiv 0 \tag{3.6}$$

Hence, summing (3.5) over i implies that through first order in polymer concentration

$$\boldsymbol{D}(t - t') = 0 \tag{3.7}$$

and hydrodynamic screening vanishes for an individual *phantom* chain[21] with full unaveraged hydrodynamic interactions. Note that the use of (3.6) in (3.5) is predicted on the fact that $\langle \boldsymbol{g}_{jm}(t,t'|\{\mathbf{r}_p(\tau)\})\rangle$ is bounded. This follows from the physical requirement that the average linear response of a polymer, $\delta\langle\mathbf{R}_{j\beta}(t)\rangle$, to a constant applied force be bounded. The violation of this condition would imply the existence of an instability and very likely the inapplicability of the original model of the chain dynamics.

B. Dynamic Intrinsic Viscosity in the Preaveraging Approximation. The coefficient of $\mathbf{k}^2$ in $\Sigma(k, t - t')$ may be obtained by expanding the exponential in powers of $\mathbf{k}$ via

$$\exp\{i\mathbf{k}\cdot[\mathbf{r}_i(t) - \mathbf{r}_m(t')]\} = 1 - i\mathbf{k}\cdot[\mathbf{r}_i(t) - \mathbf{r}_m(t')] - \\ \tfrac{1}{2}\mathbf{kk}:[\mathbf{r}_i(t) - \mathbf{r}_m(t')][\mathbf{r}_i(t) - \mathbf{r}_m(t')] + O(\mathbf{k}^3) \tag{3.8}$$

The isotropy of the averaged polymer solution implies the absence of any preferred direction in space. Consequently, the configurational averaging in (3.4) must produce a function of $k^2 = |\mathbf{k}|^2$. The contribution of the odd powers of $\mathbf{k}$ in (3.8) to the average (3.4) must therefore vanish. The term in $\mathbf{kk}$:... in (3.8) after averaging must be replaced by the factor $-{}^1/{}_6\mathbf{k}^2[\mathbf{r}_i(t) - \mathbf{r}_m(t')]^2$, etc. Thus, the polymer contribution to the viscosity is given by

$$\delta\eta(t - t')\boldsymbol{1} = \\ -(N/6V)\sum_{i,j,m} \kappa A_{ij}\langle[\mathbf{r}_i(t) - \mathbf{r}_m(t')]^2\boldsymbol{g}_{jm}(t,t'|\{\mathbf{r}_p(\tau)\})\rangle + O(c^2) \tag{3.9}$$

The complexity of $\boldsymbol{g}_{jm}(t,t'|\{\mathbf{r}_p\})$ discussed in section 2 leads us now to invoke the popular preaveraging approximation[2,3,6] of replacing $\boldsymbol{G}[\mathbf{R}_{j\beta}(t) - \mathbf{R}_{i\beta}(t)]$ in (2.19) by its average

$$\langle \boldsymbol{G}[\mathbf{r}_j(t) - \mathbf{r}_i(t)]\rangle \equiv \zeta^{-1}\boldsymbol{1}H_{ji} \tag{3.10}$$

The resultant approximate $\boldsymbol{g}_{jm}{}^{pa}$ is now independent of the $\{\mathbf{r}_p\}$, and it is a function of $t - t'$. The equation for the preaveraged $\boldsymbol{g}_{jm}{}^{pa}$

$$\left\{\frac{\partial}{\partial t}\boldsymbol{1}\delta_{jp} + \sum_i \zeta^{-1}\boldsymbol{1}H_{ji}\kappa A_{ip}\right\}\boldsymbol{g}_{pm}{}^{pa}(t,t') = \delta_{jm}\boldsymbol{1}\delta(t - t') \tag{3.11}$$

may be solved formally to give

$$\boldsymbol{g}_{pm}{}^{pa}(t,t') \equiv g_{pm}{}^{pa}(t - t')\boldsymbol{1} = \\ \boldsymbol{1}\theta(t - t')(\exp[-\zeta^{-1}\kappa\mathbf{HA}(t - t')])_{pm} \tag{3.12}$$

where the exponential contains the matrix $\mathbf{HA}$ of the Rouse–Zimm theory and $\theta(x)$ is the step function.

Using (3.12) in (3.9) gives the preaveraging approximation

$$\delta\eta^{pa}(t-t') = -(N/6V)\sum_{i,j,m}\kappa A_{ij}\langle[\mathbf{r}_i(t)-\mathbf{r}_m(t')]^2\rangle\theta(t-t')\times \{\exp[-\zeta^{-1}\kappa\mathbf{HA}(t-t')]\}_{jm} \quad (3.13)$$

The quadratic expression may be expanded to give the summand

$$\kappa A_{ij}[\langle|\mathbf{r}_i(t)|^2\rangle + \langle|\mathbf{r}_m(t')|^2\rangle - 2\langle\mathbf{r}_i(t)\cdot\mathbf{r}_m(t')\rangle]\times \{\exp[-\zeta^{-1}\kappa\mathbf{HA}(t-t')]\}_{jm} \quad (3.14)$$

When the second term of (3.14) is summed over i, we have an overall factor of $\sum_i A_{ij}$ which vanishes by (3.6). The first term of (3.4) contributes a factor of $\sum_m\{\exp[-\zeta^{-1}\kappa\mathbf{HA}(t-t')]\}_{jm}$, which is now demonstrated to likewise vanish. Expanding the exponential in powers of $t-t'$ gives

$$\sum_m[\delta_{jm} - \zeta^{-1}\kappa\sum_a H_{ja}A_{am}(t-t') + \tfrac{1}{2}(\zeta^{-1}\kappa)^2\sum_{a,b,c}H_{ja}A_{ab}H_{bc}A_{cm}(t-t')^2 + ...] \quad (3.15)$$

It is clear that the last matrix factor in each term of (3.15) apart from the first is one in $A_{\cdot m}$, where the dot designates some dummy summation index. Hence, the last matrix factor of $\sum_m A_{\cdot m}$ makes all these terms vanish. The remaining portion arising from the first term in (3.15) gives $\kappa A_{ij}\langle|\mathbf{r}_i(t)|^2\rangle$, which vanishes when summed over j because $\sum_j A_{ij} = 0$ by (3.6). Thus, (3.13) is reduced to the correlation function form

$$\delta\eta^{pa}(t-t') = (N/3V)\sum_{i,j,m}\kappa A_{ij}\langle\mathbf{r}_i(t)\cdot\mathbf{r}_m(t')\rangle\theta(t-t')\times \{\exp[-\zeta^{-1}\kappa\mathbf{HA}(t-t')]\}_{jm} + O(c^2) \quad (3.16)$$

From (2.10a) and the definition of the dynamic intrinsic viscosity $[\eta(\omega)]$

$$\delta\eta(\omega) = c\eta_0[\eta(\omega)] + O(c^2) \quad (3.17)$$

with the polymer mass concentration given as

$$c = M_A Nn/VN_A \quad (3.18)$$

where M_A is the monomer molecular weight and N_A is Avogadro's number, the preaveraged intrinsic viscosity is

$$[\eta(\omega)] = \lim_{\epsilon\to0^+}\frac{\kappa N_A}{3M_A n\eta_0}\sum_{i,j,m}A_{ij}\int_0^\infty d\tau\,\exp(-i\omega\tau-\epsilon\tau)\times \langle\mathbf{r}_i(\tau)\cdot\mathbf{r}_m(0)\rangle[\exp(-\zeta^{-1}\kappa\mathbf{HA}\tau)]_{jm} \quad (3.19)$$

C. Proof of Equivalence of (3.19) and Rouse–Zimm Preaveraged Theory. To continue further it is necessary to evaluate the single-chain correlation function $\langle\mathbf{r}_i(t)\cdot\mathbf{r}_m(0)\rangle$. It should be noted that an alternative approach involves substituting the preaveraging approximation (3.12) for g_{jm} into (3.4). Then the average to be determined is $\langle\exp\{i\mathbf{k}\cdot[\mathbf{r}_i(t) - \mathbf{r}_m(t')]\}\rangle$. n^{-2} times the sum of this quantity over i and m is just the dynamic single-chain structure factor given by Pecora.[22,23] This enables the evaluation of the leading order c part of $\Sigma(\mathbf{k}, t-t')$ from which the viscosity is readily extracted. As this method produces the full $\Sigma(\mathbf{k}, t-t')$, which is of interest in calculating the Huggins coefficient, the Burnett coefficients, etc., this calculation will be presented elsewhere.[20]

We consider a single chain in a fluid at equilibrium (in a frame moving with the center of mass, for convenience). Within the preaveraging approximation the equation of motion (2.17) for this chain reduces to

$$\dot{\mathbf{r}}_j(t) + \sum_{i,m}\kappa\zeta^{-1}H_{ji}A_{im}\mathbf{r}_m(t) = \mathbf{v}^*(\mathbf{r}_j(t),t) \quad (3.20)$$

where $\mathbf{v}^*$ are the random velocity fluctuations in the fluid that drive the Brownian motion of the chain. Equation 3.20 has the formal solution

$$\mathbf{r}_j(t) = \int_{t_0}^{t}dt_1\,g_{ji}^{pa}(t-t_1)\mathbf{v}^*(\mathbf{r}_i(t_1),t_1) \quad (3.21)$$

Forming $\langle\mathbf{r}_i(t)\cdot\mathbf{r}_m(t')\rangle$ and using the preaveraged form of (2.5a)

$$\langle v_\lambda^*(\mathbf{r}_i(t),t)v_\mu^*(\mathbf{r}_j(t'),t')\rangle = 2\delta_{\lambda\mu}k_BT\zeta^{-1}H_{ij}\delta(t-t') \quad (3.22)$$

enable us to find

$$\langle\mathbf{r}_i(t)\cdot\mathbf{r}_m(t')\rangle = 6k_BT\sum_{q,p}\int_{t_0}^{\infty}dt_1\,g_{iq}^{pa}(t-t'-t_1)\zeta^{-1}H_{qp}g_{mp}^{pa}(-t_1) \quad (3.23)$$

For an equilibrium system the initial time can be taken to $-\infty$, so (3.19) is reduced to the matrix form

$$[\eta(\omega)] = \lim_{\epsilon\to0^+}\frac{2\kappa k_BTN_A}{M_A n\eta_0}\sum_{i,j,m,p,q}A_{ij}\int_0^\infty d\tau\,\exp(-i\omega\tau-\epsilon\tau)\times \int_{-\infty}^{0}dt_1\,[\exp(-\zeta^{-1}\kappa\mathbf{HA}(\tau-t_1))]_{iq}\times \zeta^{-1}H_{qp}[\exp(-\zeta^{-1}\kappa\mathbf{HA}\tau)]_{jm}[\exp(\zeta^{-1}\kappa\mathbf{HA}t_1)]_{mp} \quad (3.24)$$

Equation 3.24 may be simplified further by considering the well-known transformation $\mathbf{Q}$ diagonalizing $\mathbf{H}$ and $\mathbf{A}$. Introduce the diagonals $\mathbf{M}$ and $\mathbf{N}$ with diagonal elements μ_a and ν_a, respectively. Then as summarized by Yamakawa[3]

$$\mathbf{Q}^T\mathbf{AQ} = \mathbf{M}$$
$$\mathbf{Q}^{-1}\mathbf{H}(\mathbf{Q}^{-1})^T = \mathbf{N} \quad (3.25)$$

This enables us to write, for instance

$$[\exp(-\zeta^{-1}\kappa\mathbf{HA}\tau)]_{jm} = \sum_a Q_{ja}\exp(-\zeta^{-1}\kappa\mu_a\nu_a\tau)(Q^{-1})_{am} \quad (3.26)$$

Substitution of (3.26) into (3.24) and repeated use of (3.25) and (3.26) convert (3.24) to

$$\begin{aligned}[\eta(\omega)] &= \lim_{\epsilon\to0^+}\frac{2k_BTN_A}{M_A n\eta_0}\sum_a\kappa\zeta^{-1}\mu_a\nu_a\int_0^\infty d\tau\int_{-\infty}^{0}dt_1\,\exp[-i\omega\tau-\epsilon\tau-2\zeta^{-1}\kappa\mu_a\nu_a(\tau-t_1)] \\ &= \lim_{\epsilon\to0^+}\frac{k_BTN_A}{M_A n\eta_0}\sum_a[\epsilon+i\omega+2\zeta^{-1}\kappa\mu_a\nu_a]^{-1} \\ &= \frac{k_BTN_A}{M_A n\eta_0}\sum_a\frac{\tau_a}{1+i\omega\tau_a}\end{aligned} \quad (3.27)$$

The well-known preaveraged Rouse–Zimm relaxation times are

$$\tau_a = (2\zeta^{-1}\kappa\mu_a\nu_a)^{-1}$$

and (3.27) is the corresponding *exact* Rouse–Zimm preaveraged dynamic intrinsic viscosity.[2,3] This demonstrates the formal identity of the multiple scattering and Rouse–Zimm dynamic intrinsic viscosities. The importance of the Freed–Edwards theory, however, resides in its ability to treat polymer solutions at nonzero concentrations.

4. Hydrodynamic Screening for Phantom Chains at $c \neq 0$

The vanishing of $\Sigma(k = 0, t-t')$ to all orders in concentration for phantom chains can be demonstrated by treating an arbitrary term in the multiple scattering expansion (2.25) of the form

$$\sum_{\alpha}\sum_{\beta\neq\alpha}\dots\sum_{\omega\neq\dots}\langle \boldsymbol{T}_\alpha\cdot\boldsymbol{G}\cdot\boldsymbol{T}_\beta\cdot\boldsymbol{G}\cdot\dots\cdot\boldsymbol{T}_\omega\rangle \tag{4.1}$$

The integrations and summations are understood to be implied for notational brevity. Substituting the definition (2.24) for the $\boldsymbol{T}$ operators and performing all the spatial ($\mathbf{r}$, $\mathbf{r}'$, ...) integrations convert (4.1) into the contribution to $\Sigma(\mathbf{r}-\mathbf{r}',t-t')$

$$\pm\sum_{\alpha}\sum_{\beta\neq\alpha}\dots\sum_{\omega\neq\dots}\langle\delta(\mathbf{r}-\mathbf{R}_{\alpha i}(t))\kappa A\boldsymbol{g}_\alpha\cdot G(\mathbf{R}_{\alpha j}-\mathbf{R}_{\beta l})\kappa A\cdot\boldsymbol{g}_\beta\cdot \boldsymbol{G}(\mathbf{R}_{\beta m}-\mathbf{R}_{\gamma p})\cdot\dots\boldsymbol{G}(\dots-\mathbf{R}_{\omega y})\kappa A\cdot\boldsymbol{g}_\omega\delta(\mathbf{r}'-\mathbf{R}_{\omega z}(t'))\rangle \tag{4.2}$$

where $\boldsymbol{g}$ is shorthand for $\boldsymbol{g}_{ij}(t,t'|\{\mathbf{r}_{\alpha q}\})$, etc.

We consider first the configurational average over the polymer center-of-mass positions $\{\mathbf{R}_\alpha{}^0\}$. Introduce the spatial Fourier transforms of the two Dirac δ functions and the $\boldsymbol{G}$ factors to convert (4.2) into

$$\pm\prod_{\lambda=1}^{n_t}\left[\int\frac{\mathrm{d}^3k_\lambda}{(2\pi)^3}\right]\exp(i\mathbf{k}_1\cdot\mathbf{r}+i\mathbf{k}_{n_t}\cdot\mathbf{r}')\times \langle\exp[-i\mathbf{k}_1\cdot\mathbf{R}_{\alpha i}(t)]\kappa A\boldsymbol{g}_\alpha\cdot\exp[i\mathbf{k}_2\cdot(\mathbf{R}_{\alpha j}-\mathbf{R}_{\beta l})]\,\boldsymbol{G}(\mathbf{k}_2)\kappa A\cdot\boldsymbol{g}_\beta\times \exp[i\mathbf{k}_3\cdot(\mathbf{R}_{\beta m}-\mathbf{R}_{\gamma p})]\cdot\boldsymbol{G}(\mathbf{k}_3)\dots\boldsymbol{G}(\mathbf{k}_{n_t-1})\times \exp[i\mathbf{k}_{n_t-1}\cdot(\dots-\mathbf{R}_{\omega y})]\kappa A\cdot\boldsymbol{g}_\omega\exp[-i\mathbf{k}_{n_t}\cdot\mathbf{R}_{\omega z}(t')]\rangle \tag{4.3}$$

where $\boldsymbol{G}(\mathbf{k})$ can be shown to be[4,6]

$$\boldsymbol{G}(\mathbf{k})=(\boldsymbol{1}-k^{-2}\mathbf{k}\mathbf{k})/\eta_0k^2 \tag{4.4}$$

According to (2.19) and the equations which follow, $\boldsymbol{g}_\alpha$ is independent of the center-of-mass $\mathbf{R}_\alpha{}^0$ of chain α. Hence, the only terms in (4.3) which are associated with center-of-mass positions are contained in the factor

$$\langle\exp(-i\mathbf{k}_1\cdot\mathbf{R}_\alpha{}^0)\exp[i\mathbf{k}_2\cdot(\mathbf{R}_\alpha{}^0-\mathbf{R}_\beta{}^0)]\exp[i\mathbf{k}_3\cdot(\mathbf{R}_\beta{}^0-\mathbf{R}_\gamma{}^0)]\dots\exp[i\mathbf{k}_{n_t-1}\cdot(\dots-\mathbf{R}_\omega{}^0)]\exp(-i\mathbf{k}_{n_t}\cdot\mathbf{R}_\omega{}^0)\rangle \tag{4.5}$$

The center-of-mass average for *phantom* polymer chains involves the distribution function

$$\prod_{\beta=1}^{N}\left[\int\mathrm{d}\mathbf{R}_\beta{}^0/V\right] \tag{4.6}$$

while for correlated, phantom chains we have the distribution function

$$\prod_{\beta=1}^{N}\left[\int\mathrm{d}\mathbf{R}_\beta{}^0/V\right]P(\{\mathbf{R}_\beta{}^0\}) \tag{4.7}$$

where $P(\{\mathbf{R}_\beta{}^0\})$ depends only on interparticle separations. [The dependence of $P(\{\mathbf{R}_\beta{}^0\})$ on the internal coordinates $\{\mathbf{r}_{\beta j}\}$ is not separable, but that point is of no concern at this juncture.] In both (4.6) and (4.7) we transform to the set of relative coordinates

$$\rho_\alpha=\mathbf{R}_\alpha{}^0 \qquad \rho_\beta\equiv\mathbf{R}_\beta{}^0-\mathbf{R}_\alpha{}^0 \qquad \text{all }\beta\neq\alpha \tag{4.8}$$

All distribution functions depend only on $\{\rho_\beta|\beta\neq\alpha\}$ and are *independent* of $\mathbf{R}_\alpha{}^0$. The integrations are transformed as

$$\prod_{\beta=1}^{N}\left[\int\mathrm{d}\mathbf{R}_\beta{}^0/V\right]=\left(\int\mathrm{d}\rho_\alpha{}^0/V\right)\prod_{\beta(\neq\alpha)=1}^{N}\left[\int\mathrm{d}\rho_\beta{}^0/V\right] \tag{4.9}$$

Using (4.8) transforms (4.5) to

$$\langle\exp(-i\mathbf{k}_1\cdot\rho_\alpha)\exp[i\mathbf{k}_2\cdot(-\rho_\beta)]\exp[i\mathbf{k}_3\cdot(\rho_\beta-\rho_\gamma)]\dots\exp[i\mathbf{k}_{n_t-1}\cdot(\dots-\rho_\omega)]\exp[-i\mathbf{k}_{n_t}\cdot(\rho_\omega+\rho_\alpha)]\rangle \tag{4.10}$$

Note that because only the first and the last factors in (4.5) do *not* involve relative positions, they are the *only ones* in (4.10) which produce factors containing ρ_α. The integral of (4.10) over ρ_α is now trivial, giving $(2\pi)^3\delta(\mathbf{k}_1+\mathbf{k}_{n_t})$. When this is inserted back into (4.3) and used to evaluate the $\mathbf{k}_{n_t}$ integral, the ($\mathbf{r}$ and $\mathbf{r}'$)-dependent factor becomes $\exp[i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')]$. This is trivially a statement of the isotropy of space and the resultant fact that Σ depends on $\mathbf{r}-\mathbf{r}'$.

Having performed only the $\int\mathrm{d}\mathbf{R}_\alpha{}^0=\int\mathrm{d}\rho_\alpha$, we may now denote $\langle\,\rangle_{\mathbf{R}_\alpha{}^0=0}$ as the restricted average, where $\mathbf{R}_\alpha{}^0$ is taken as 0. To obtain $\Sigma(\mathbf{k}=0,t-t')$ we utilize the result of the $\int\mathrm{d}\mathbf{R}_\alpha{}^0$ integral and take the spatial Fourier transform of (4.3). The $\boldsymbol{k}=0$ contribution thereby provided is found to be

$$\pm\prod_{\lambda=2}^{n_t-1}\left[\int\frac{\mathrm{d}^3k_\lambda}{(2\pi)^3}\sum_{i,j,\dots}\kappa A_{ij}\langle\boldsymbol{g}_\alpha\times \exp[i\mathbf{k}_2\cdot(\mathbf{r}_{\alpha j}-\mathbf{R}_{\beta l})]\cdot\boldsymbol{G}(\mathbf{k}_2)\kappa A\boldsymbol{g}_\beta\exp[i\mathbf{k}_3\cdot(\mathbf{R}_{\beta m}-\mathbf{R}_{\gamma p})]\cdot \boldsymbol{G}(\mathbf{k}_3)\dots\boldsymbol{G}(\mathbf{k}_{n_t-1})\exp[i\mathbf{k}_{n_t-1}\cdot(\dots-\mathbf{R}_{\omega y})]\kappa A\cdot\boldsymbol{g}_\omega\rangle\right]_{\mathbf{R}_\alpha{}^0=0} \tag{4.11}$$

Notice that the choice of $\mathbf{k}$ $(=\mathbf{k}_1=\mathbf{k}_{n_t})=0$ eliminates the first and last factors in angular brackets in (4.3). Now, the coefficient of the angular brackets in (4.11) contains the left-most term $\sum_iA_{ij}$ which vanishes by (3.6). Hence, $\Sigma(\mathbf{k}=0,t-t')$ vanishes term by term in the multiple scattering expansion for *phantom* chains. This implies that there is not hydrodynamic screening for *phantom* chains to all orders in concentrations with full, unaveraged, anisotropic hydrodynamic interactions.

5. Model for Hydrodynamic Screening

It is obvious that it is possible to take *real* non-cross-linked, linear polymer molecules and form them into a very porous medium through which fluid may flow. Darcy's law must hold for such a porous material, apart, perhaps, for some corrections due to nonhomogeneous flow. This, however, implies that hydrodynamic screening is present in this dense polymer system. As the screening is absent for these real chains at inifinite dilution, there must be an onset of hydrodynamic screening at some nonzero concentrations.[10] This onset is due to the presence of interactions and entanglements in real polymer systems. In the theoretically interesting, but experimentally unfeasible, limit of a *very* high molecular weight *linear* polymer, where a *single chain* can provide a macroscopic porous sample, hydrodynamic screening is therefore also present due to the self-entanglements.

Let us assume that at a concentration c of polymer chains there is a fraction f_e which are entangled. f_e, in general, is a function of frequency ω. A theory of f_e may be designed on the basis of encounter probabilities as reviewed by Graessley.[24] This implies that f_e varies with c and molecular weight M as

$$f_\mathrm{e}\propto cM \tag{5.1}$$

Above some "critical" concentration $c_\mathrm{h}{}^*$, f_e becomes equal to unity. Intuitively, it is to be expected that $c_\mathrm{h}{}^*$ is proportional to c^*, the chain overlap concentration. Thus, in the semidilute region the free center-of-mass motion of any chain is ultimately impeded by the presence of entanglements with another chain.

A full mathematical theory of polymer dynamics with entanglements is currently unavailable, so a model must be invoked. We consider here a chain with n units where some interior unit E is trapped in an entanglement junction. The unit is modeled by taking $\mathbf{r}_\mathrm{E}(t)$ to be fixed at the position of the entanglement junction $\mathbf{r}_\mathrm{E}$, independent of time. A slightly more general model would allow of oscillations of $\mathbf{r}_\mathrm{E}(t)$ about an equilibrium value $\mathbf{r}_\mathrm{E}$. At a concentration c of polymers this entangled test chain has an effective concentration-dependent hydrodynamic interaction tensor $\zeta^{-1}\hat{H}_{ij}(c)$ between units i and j on the chain. The effective medium theory of the hydrodynamics of polymer solutions can be introduced in the discrete representation of section 2, with a fraction f_e of the chains having these entanglement junctions. We dispense here with the detailed derivation of the effective medium theory[7] and merely note that it requires that the calculation be performed with $\zeta^{-1}\hat{H}_{ij}(c)$ for a single chain to calculate $\Sigma(\mathbf{k},\omega;c)$. Then this $\Sigma(\mathbf{k},\omega;c)$ is used to determine $\zeta^{-1}\hat{H}_{ij}(c)$ self-consistently. Here it is unnecessary to treat the self-consistent solution, as only a qualitative phenomenological description is desired.

The solution has a fraction f_e of entangled chains, so the friction coefficient density tensor, the "self-energy", for the solution is a weighted average from the entangled and nonentangled chains

$$\Sigma_{\text{soln}} = f_e\Sigma_{\text{ent}} + (1 - f_e)\Sigma_{\text{non-ent}} \tag{5.2}$$

$\Sigma_{\text{non-ent}}$ is calculated by using a Rouse bead-spring model with the effective hydrodynamic interaction tensor $\zeta^{-1}\hat{H}_{ij}(c)$ (which depends on Σ_{soln}). The parameters ζ, l, etc. may become concentration dependent. Nevertheless, even without the explicit specification of $\hat{H}_{ij}(c)$, the arguments of section 3 show that $\Sigma_{\text{non-ent}}(\mathbf{k} = 0, t - t') \equiv 0$, so the nonentangled chains do not contribute to hydrodynamic screening. The specific viscosity per chain has the same form as (3.27) except that the τ_a are evaluated from the diagonal matrix elements of $\hat{\mathbf{Q}}^{-1}\hat{\mathbf{H}}(c)(\hat{\mathbf{Q}}^{-1})^{\mathrm{T}}$ so the τ_a become concentration dependent. The leading c dependence of the τ_a has been given by Muthukumar and Freed.[9] Hence, we may dispense with a consideration of $\Sigma_{\text{non-ent}}$.

The evaluation of Σ_{ent} requires a description of the dynamics of at least a pair of entangled polymer chains. As the treatment of even the equilibrium properties of entangled polymers is extremely difficult, here we introduce a phenomenological model to qualitatively describe the properties of Σ_{ent}. Concepts here are borrowed from the theory of rubber elasticity by treating the entanglements as temporary linkages (either fixed or slip-links) between the chains. Each entanglement is taken to introduce two new polymer strands. Of the N initial chains of n units a fraction f_e are $(1/2)f_eN$. Approximating this in terms of binary entanglements at low concentrations, this implies $(1/2)f_eN$ entanglements between f_eN primary chains, resulting in $2f_eN$ strands of average polymerization index $n/2$. At higher concentrations the f_eN primary chains have m entanglements, and the individual strands have an average polymerization index

$$n_{\text{eff}} = \frac{f_eNn - 2m}{f_eN + 2m} \tag{5.3}$$

These $f_eN + 2m$ strands with n_{eff} units on average are then taken as individual Rouse chains with the same screened hydrodynamic interaction tensor $\zeta^{-1}\hat{H}_{ij}(c)$. Thus, these strands do not contribute to hydrodynamic screening.

In the simplest possible model the entanglement junctions are temporarily taken to be immobile. Hence, there are at least $2m$ units which are fixed because of the m entanglement constraints. This simple limit[14] produces a net retarding force on the fluid motion and, consequently, provides a contribution to the $\mathbf{k} = \omega = 0$ limit of Σ_{ent} of

$$f_e\Sigma_{\text{ent}}(\mathbf{k} = \omega = 0) = -\frac{2m(c)}{V}\zeta_{\text{ent}}(c) \tag{5.4}$$

where $m(c)$ is the concentration-dependent number of entanglements and $\zeta_{\text{ent}}(c)$ is the friction coefficient for the junction units. When the entangled units are allowed to fluctuate, the contribution of this motion to the $\mathbf{k}^2$ part of Σ_{ent} contains [cf. (3.13)] the correlation function

$$C_{\mathrm{E}}(t - t') = \langle[\mathbf{r}_{\mathrm{E}}(t) - \mathbf{r}_{\mathrm{E}}(t')]^2\rangle \tag{5.5}$$

In the limit of high concentration these fluctuations become damped out, and the $C_{\mathrm{E}}(t - t')$ contribution becomes negligible compared to that of the hydrodynamically screened strands between entanglement junctions. Furthermore, for $c > c_{\mathrm{h}}^*$ we have $f_e = 1$, so the resultant viscosity is that of $N + 2m$ Rouse strands with $(Nn - 2m)/(N + 2m)$ units on average and screened hydrodynamic interactions as produced by (5.4). (We assume here that the primary strands are short enough that a macroscopically entangled network is *not* formed.) The number of entangled units $m(c)$ grows with concentration, so the hydrodynamic screening becomes progressively larger. Given the model of $N + 2m$ strands with the screening constrained by (5.4), the techniques of Freed and Edwards[5,6] show that the high-concentration limiting viscosity is of the Rouse form with an effective concentration-dependent friction coefficient. The results of Freed and Edwards for this case may be reinterpreted as a mathematical model in which the unknown $\Sigma_{\text{ent}}(\mathbf{k} = \omega = 0)$ is calculated self-consistently from the effective medium theory rather than by a true microscopic description. The final results, however, are qualitatively the same in the high-concentration limit, where the calculations of Freed and Edwards are given.[5,6] On the contrary, the present model shows that $\Sigma_{\text{ent}}(\mathbf{k} = \omega = 0)$ at low concentration varies with concentration at least with a second-power law, while the Freed–Edwards self-consistent method calculation gives an unphysical first-power dependence.

As is well-known in the study of the dynamics of networks, the relaxation times should be calculated for the network as a whole and not for the strands and junctions separately. Methods such as those given recently by Graessley[25] might be adaptable to entangled systems by treating the entanglements as slip-linkages following Edwards.[26] This difficult task is left for a future study.

6. Discussion

The multiple scattering representation of the concentration dependence of the hydrodynamics of polymer solutions is reformulated by using a discrete polymer chain model in order to facilitate comparisons with the Rouse–Zimm theory in the limit of infinite dilution and to alleviate previous difficulties with subtle mathematical limiting procedures involved in obtaining the long-chain, long-wavelength, low-frequency dynamical properties of polymer solutions.

The discrete chain representation enables us to prove that hydrodynamic screening is absent within a single *phantom* polymer chain. This theorem then enables us to transform the multiple scattering theory correlation function for the dynamic intrinsic viscosity identically into the corresponding Rouse–Zimm form when the preaveraging approximation is invoked. It is further proven that hydrodynamic screening likewise vanishes identically order by order in the multiple scattering expansion and, hence, order by order in concentration for *phantom chains*. As hydrodynamic screening is responsible for the transition from a low-concentration Rouse–Zimm-like dependence of the intrinsic viscosity to a high-concentration Rouse-like limit, the physical origins of this transition must arise from the departure of the polymers from phantom chains. A resolution of this question may be deduced from the results of recent studies of the concentration dependence of the hydrodynamics of suspensions of spheres.[14,15]

Spheres at low concentrations are free to drift with the local perturbed fluid velocity as averaged over the surface of the sphere. Hence, there is not hydrodynamic screening in this case. At high concentration the sphere–sphere interactions impede the unrestricted ability of the spheres to drift with the fluid, and at sufficiently high sphere concentration the motion of the spheres is largely frozen out, with the spheres becoming a randomly packed glass-like system. A Darcy's law net retarding force[12] is present for flow through this porous sphere glass. By definition this implies the presence of hydrodynamic screening and a transition to nonzero hydrodynamic screening at some intermediate sphere concentration.

The physical situation in polymer solution must then be analogous. The polymers are spread out over a wider volume, and their random coil nature leads to entanglements well before the concentration is sufficient to produce a nonflowing porous polymer plug. These entanglements thus impede the ability of the polymer chains to drift with the fluid[27] and thereby produce hydrodynamic screening. A simple phenomenological model is introduced to described qualitatively this effect. The results at high concentration are in general qualitative accord with the self-consistent calculations of Freed and Edwards,[5,6] but the hydrodynamic screening obtained here is considerably reduced at low concentration. Although the discussion is limited to low enough concentrations and/or short enough chains where a 3.4 power law for the viscosity is not to be observed, this model of hydrodynamic screening may be of relevance to the description of the entangled limit. Tracer chain diffusion proceeds in entangled polymer systems by a reptation motion.[28] If the reptation time were the longest relaxation time, then the viscosity would vary with molecular weight M as an M^3 law. However, entanglements may impede the motion of some of the chains, freezing out reptation for these chains. (This occurs for starlike polymers.) Hence, the motion of these chains must involve a cooperative venture, and this could, perhaps, lead to a higher molecular weight dependence than an M^3 power law. This speculation should be considered through further experimental and theoretical study.

Acknowledgment. This research is supported, in part, by NSF Grant DMR78-26630 (Polymers Program).

References and Notes

(1) Rouse, P. E., Jr. *J. Chem. Phys.* **1953**, *21*, 1272.
(2) Zimm, B. H. *J. Chem. Phys.* **1956**, *24*, 269.
(3) For a review, see: Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(4) Edwards, S. F.; Freed, K. F. *J. Chem. Phys.* **1974**, *61*, 1189.
(5) Freed, K. F.; Edwards, S. F. *J. Chem. Phys.* **1974**, *61*, 3626. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 2025. *J. Chem. Phys.* **1975**, *62*, 4032.
(6) Freed, K. F. In "Progress in Liquid Physics"; Croxton, C. A., Ed.; Wiley: London, 1978; p 343.
(7) Freed, K. F.; Metiu, H. *J. Chem. Phys.* **1978**, *68*, 4604.
(8) Muthukumar, M.; Freed, K. F. *Macromolecules* **1977**, *10*, 899.
(9) Muthukumar, M.; Freed, K. F. *Macromolecules* **1978**, *11*, 843.
(10) Freed, K. F. *Ferroelectrics* **1980**, *30*, 277.
(11) Perico, A.; Cuniberti, C. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1983.
(12) Brinkman, H. C. *Appl. Sci. Res., Sect. A* **1947**, *1*, 27, 81.
(13) Muthukumar (private communication) has obtained similar results from the analysis of the simple model of a rigid random coil chain within the multiple scattering theory. This model has the virtue of only containing six degrees of freedom associated with the translation and rotation of the polymer. An average is performed over the random coil configurations at the end of the calculations. This model is expected to be useful in the zero-frequency limit when internal chain motions are irrelevant. The proof given in this paper, however, includes the Brownian chain dynamics and is therefore applicable to the full frequency domain over which the Rouse–Zimm model is applicable.
(14) Freed, K. F.; Muthukumar, M. *J. Chem. Phys.* **1978**, *68*, 2088. Muthukumar, M.; Freed, K. F. *Ibid.* **1979**, *70*, 5875.
(15) Freed, K. F.; Muthukumar, M. *J. Chem. Phys.* **1978**, *69*, 2657. *Ibid.*, submitted for publication.
(16) The calculated Huggins coefficients should be $^1/_2$ those given in ref 5, 6, 8, and 9 within the self-consistent approximations used there. This point has also been noted by Muthukumar (private communication).
(17) Technical precision would require the retention of the $\rho_0(\partial/\partial t)$ term and the resultant explicit time dependence of the dynamical Oseen tensor [instead of the zero-frequency limit in (2.11)] in order to apply (2.5). Then the zero-frequency limit of (2.11) can be utilized after the averages (2.5) are introduced. For the low frequencies of interest here, $\omega \lesssim 10^6$ Hz, the dynamics of the Oseen tensor is irrelevant,[4,6] so we simplify matters by using the zero-frequency limit and the correlation function (2.5a) to properly describe the effects of the random fluid fluctions in driving the Brownian motion of the polymer.
(18) An alternative justification of this ϵ-limiting procedure is given by: Berne, B. J.; Harp, G. D. *Adv. Chem. Phys.* **1970**, *17*, 63.
(19) Perico, A.; Piaggio, P.; Cuniberti, C. *J. Chem. Phys.* **1975**, *62*, 4911.
(20) Perico, A.; Freed, K. F., to be submitted for publication.
(21) Freed and Edwards[5,6] consider the Fourier transform of (3.5) in the preaveraging approximation without the important ϵ limits in (2.10b). This Fourier integral yields the singular term $A_{js}^{-1}H_{sm}^{-1}$ to produce an *apparent* nonzero value of $\boldsymbol{D}(\omega = 0)$. However, it is clear that $\boldsymbol{D}(t - t')$ of (3.5) vanishes identically, so its Fourier transform must likewise vanish. This example emphasizes the importance of the casuality-induced ϵ limits in (2.10) when orders of integration are interchanged.
(22) Berne, B. J.; Pecora, R. "Dynamic Light Scattering"; Wiley: New York, 1976; pp 176–7. Pecora, R. *J. Chem. Phys.* **1965**, *43*, 1562.
(23) Perico, A.; Piaggio, P.; Cuniberti, C. *J. Chem. Phys.* **1975**, *62*, 2690.
(24) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 1. Pearson, D. S.; Graessley, W. W. *Macromolecules* **1978**, *11*, 528.
(25) Graessley, W. W. *Macromolecules* **1980**, *13*, 372.
(26) Ball, R. C.; Edwards, S. F. *Macromolecules* **1980**, *13*, 748.
(27) Yu, T. L.; Reihanian, H.; Jamieson, A. M. *Macromolecules* **1980**, *13*, 1590. Nose, T.; Chu, B. *Ibid.* **1979**, *12*, 590.
(28) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789, 1802, 1818. de Gennes, P. G. *J. Chem. Phys.* **1971**, *55*, 572. Klein, J. *Nature (London)* **1978**, *271*, 143.