$$I_{1,2}(q) = \frac{2\pi}{\eta}\int_0^\infty \mathrm{d}K \left(\frac{K}{2q}\,\frac{K^2+q^2}{q^2}\,\ln\frac{|K+q|}{|K-q|} - \frac{K^2}{q^2} \right) \times \left(S_{\mathrm{s}}(K) - \frac{1}{n} \right)^{1,2} \quad (24)$$

The small-q limit of this expression can be checked by expanding the logarithm in the q/K smallness parameter

$$I_{1,2}(q \rightarrow 0) = \frac{8\pi}{3\eta}\int_0^\infty \mathrm{d}K \left(S_{\mathrm{s}}(K) - \frac{1}{n} \right)^{1,2} \quad (25)$$

These integrals are evaluated analytically in the next appendix for Gaussian chains.

Appendix II

We assume a Gaussian chain model for $S_{\mathrm{s}}(K)$

$$S_{\mathrm{s}}(K) = \frac{1}{n^2}\sum_{i,j}^{n} e^{-(K^2l^2/6)|i-j|} \quad (26)$$

where l is the statistical length, introduce a dimensionless variable $x = Kl(n/6)^{1/2} = KR_{\mathrm{g}}$, and use the general identity (valid for $j \neq i$)

$$\sum_{i,j}^{n} A(|i-j|) = 2\sum_{i}^{n} (n-i)A(i) \quad (27)$$

to manipulate $I_1(q \rightarrow 0)$ to the form

$$I_1(q \rightarrow 0) = \frac{16\pi}{3\eta n^2 R_{\mathrm{g}}}\int_0^\infty \mathrm{d}x \sum_{i}^{n} e^{-x^2 i/n}(n-i) \quad (28)$$

We approximate the summation by an integration to find

$$I_1(q \rightarrow 0) = \frac{32\pi^{3/2}}{9\eta R_{\mathrm{g}}} \quad (29)$$

and similarly for $I_2(q \rightarrow 0)$

$$I_2(q \rightarrow 0) = \frac{8\pi}{3\eta}\,\frac{1}{n^4 R_{\mathrm{g}}}\int_0^\infty \mathrm{d}x \left(\sum_{i,j}^{n} e^{-x^2|i-j|/n} - \frac{1}{n} \right) \times \left(\sum_{k,l}^{n} e^{-x^2|k-l|/n} - \frac{1}{n} \right) = \frac{768\pi^{3/2}}{945\eta R_{\mathrm{g}}}(8(2^{1/2}) - 9) \quad (30)$$

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Incorporation of Excluded Volume into the Multiple-Scattering Theory of the Concentration Dependence of Polymer Dynamics

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ABSTRACT: A formal multiple-scattering solution is provided for the polymer chain dynamics, the fluid velocity field, etc., for a system of polymers at nonzero concentration with excluded volume. The analysis proceeds by the introduction of operators describing the dynamical contributions of excluded volume interactions to the polymer force constants. We evaluate the average of the fluid velocity field over the conformations of all polymers because this average velocity field may be utilized to compute the concentration-dependent dynamical viscosity and because related quantities can be used to evaluate the concentration-dependent polymer friction coefficients. The final results are in a form that bears a one-to-one correspondence with terms in the multiple-scattering expansion for Gaussian chains, thereby providing a general prescription for converting these former multiple-scattering expressions into ones incorporating excluded volume exactly. A set of preaveraging-type approximations is introduced. The simplest is shown to yield a dynamic intrinsic viscosity of the Rouse–Zimm form, but with excluded volume dependent hydrodynamic and force constant matrices. A microscopic prescription is provided for calculating the latter, while the former has been evaluated elsewhere by renormalization group methods. The same analysis, applied here to derive the excluded volume dependent viscosity, can readily be utilized to consider concentration-dependent quantities using either the concentration expansion or effective medium methods.

I. Introduction

The theory of the concentration dependence of the hydrodynamics of solutions of polymer chains has been presented in a multiple-scattering formalism based on either the pure solvent or an effective medium reference.[1-8] The former is useful for the development of a concentration expansion of the viscoelastic and frictional properties[8] of polymer solutions, and applications to a number of these properties have been given.[5,8] Of particular note is the theory of the leading concentration dependence of the relaxation times of the individual polymer modes,[5] which is in excellent agreement with recent experiments by Lodge and Schrag[9] except for some slight difference in the overall numerical factor and discrepancies at higher frequencies.[9] Improved calculations of these features are currently in progress. The effective medium representation,[1-3] on the other hand, is useful in describing the full concentration dependence, displaying the crossover from Zimm-like

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properties at low concentrations to Rouse-like ones at higher polymer concentrations.

The formal solutions of multiple-scattering theory have been presented in complete generality for the case of Gaussian polymer chains without excluded volume.[1-3,7,8] Edwards[10] has shown that these equations maintain the entanglement constraints due to the impenetrability of polymer chains, but unfortunately the rigorous preservation of these constraints requires an *exact* solution of these equations. The above statement may appear somewhat contradictory since both excluded volume and entanglements arise from the same repulsive interactions. One manifestation of these interactions is the static swelling of polymers in good solutions. In Θ solutions, on the other hand, the attractive and repulsive portions of the polymer–polymer effective interactions balance each other so there is no excluded volume; nevertheless, the polymers are still interacting. These interactions still prevent polymer chains from passing through each other and can still give rise to entanglements even when excluded volume is absent, i.e., in Θ solutions. Edwards[10] shows that our general concentration-dependent dynamical theory for Θ solutions preserves entanglement constraints because of the vanishing of the mutual diffusion coefficient between any pair of polymer segments of the same or differing chains when these segments come into contact. This strong result emerges from the theory with inertia neglected and the use of standard hydrodynamic boundary conditions. Although Edwards considers only the no-slip case, it can be shown that his conclusions persist for slip and partial slip since it is only the radial relative diffusion coefficient that must vanish on contact in order that the hydrodynamic equations preserve entanglement topologies.

Because the dynamical multiple-scattering equations maintain entanglement constraints, it is important to further generalize them to incorporate the other major effect of the polymer–polymer interactions, those produced by excluded volume. Excluded volume interactions lead to significant alterations in the polymer chain dimensions and relaxation times, and these are modified as a function of concentration. Approximate descriptions of polymer excluded volume have been included through the use of a nonuniform scaling of the polymer mode force constants[4,5] and more recently by the use of a stochastic linearization approximation.[11] The testing and development of these and improved approximations would be greatly facilitated by having a full formal multiple-scattering solution that exactly incorporates all excluded volume effects within the traditional excluded volume models.

The extension of the multiple-scattering theory to completely account for polymer excluded volume should be extremely useful in generalizing chain conformational space renormalization group methods[13-15] to describe the concentration dependence of the viscoelastic properties of polymer solutions. Single-chain dynamical renormalization group calculations have been performed by using a variety of related approaches.[16-18] Some are based on the polymer diffusion equation and have provided the dynamical exponent[16] and the longest relaxation time.[17] Another method[18] is based on the Kirkwood–Riseman approach, which cannot describe the frequency dependence due to internal chain dynamics. In principle, it should be possible to pursue the renormalization group description of excluded volume effects on the concentration dependences of viscoelastic, etc., properties of polymer solutions using a diffusion equation formalism. However, a theory of this concentration dependence has not yet been developed beginning with the traditional polymer diffusion equation[18] for the many-polymer system. Consequently, it appears more advantageous to generalize the multiple-scattering theory to incorporate excluded volume interactions. It should be noted that the Langevin-type multiple-scattering equations can always be converted to a diffusion equation, but the latter is a highly transformed version of the traditional polymer diffusion equation.[18] The Langevin-type multiple-scattering equations are similar in spirit to the Kirkwood–Riseman equations, but with equations for the internal chain dynamics appended. It is the purpose of this paper to provide this generalization of the multiple-scattering theory to fully include excluded volume and thereby to obtain exact and general correlation function expressions for the concentration-dependent dynamical viscosity with excluded volume present. Such correlation function forms may be used in numerical simulations, while their use in future renormalization group calculations may help to avoid the emergence of secular terms which plague time-dependent perturbation methods in as diverse fields as celestial and quantum mechanics. It should be emphasized that renormalization group treatments have not yet been possible for the concentration dependence of the dynamics of polymers with excluded volume and that this is expected to be a difficult task even given the formal advancements with the multiple-scattering formalism provided herein.

In the next section we describe the general model for describing polymer dynamics in solutions at nonzero concentration with excluded volume present. The multiple-scattering theory is generalized in section III to incorporate fully the excluded volume interactions, and the use of a simple identity enables the determination of the excluded volume contribution to polymer force constants in the form of a dynamical operator. After the dynamical response function for a polymer with excluded volume is introduced, the derivation of the multiple-scattering series for the fluid velocity field proceeds similarly to the case of Gaussian chains with external forces present. Upon averaging over the polymer conformations at some initial time, the interchain excluded volume interaction terms in the average fluid are shown to vanish. However, these interchain interactions affect the stochastic chain dynamics upon which the averaged fluid velocity strongly depends through the single-chain dynamical scattering kernels. (A similar theorem may be proven concerning the multiple-scattering series for the concentration dependence of the hydrodynamics of interacting spheres.) This calculated fluid velocity field immediately enables the generalization of all previous results for Gaussian chains,[1-8] using the multiple-scattering theory, to polymers with excluded volume because all properties can be derived directly from this velocity field. Hence, we do not explicitly requote all these previous results with the transcriptions for excluded volume. Some of the approximations that are available in treating these equations are described, and in particular, a preaveraging-type approximation is shown to provide a dynamical intrinsic viscosity of the Rouse–Zimm[18] form with excluded volume dependent hydrodynamic and force constant matrices defined by the derivation. A static, self-consistent approximation to these preaveraged equations has appeared previously[11] and has been used to describe excluded volume effects on the screening of hydrodynamic interactions in dilute and semidilute solutions. This is but one example of the possible applications of the more complete and generally rigorous formal theory that we develop herein. For the sake of generality it should also be noted that it is possible to include corrections to the Oseen approximation by replacing the Oseen interaction between polymer segments with one of the forms correcting for the nonzero size of the segments. The equations are presented, for simplicity, just using this Oseen approximation.

II. Model

A. Equation of Motion for Fluid. The system involves N polymer chains in a fluid of volume V with the thermodynamic limit $N \rightarrow \infty$, $V \rightarrow \infty$, $N/V \rightarrow$ constant taken at the end of the calculation. The pure fluid has density ρ_0 and viscosity η_0. If $\sigma_{i\alpha}(t)$ is the force exerted on the fluid by the ith segment on chain α at the position $\mathbf{R}_{i\alpha}(t)$, then the low shear rate dynamics is governed by the linearized Navier–Stokes equation

$$\left(\rho_0\frac{\partial}{\partial t} - \eta_0\nabla^2\right)\mathbf{v}(\mathbf{r},t) + \nabla P(\mathbf{r},t) = \sum_{i,\alpha}\delta[\mathbf{r} - \mathbf{R}_{i\alpha}(t)]\sigma_{i\alpha}(t) \tag{2.1}$$

with $\mathbf{v}(\mathbf{r},t)$ the fluid velocity at the space–time point $(\mathbf{r},t)$ and where $P(\mathbf{r},t)$ is the pressure, which is determined from the incompressibility constraint

$$\nabla\cdot\mathbf{v}(\mathbf{r},t) = 0 \tag{2.2}$$

In the low-frequency, long-chain domain of interest to us, the $\rho_0(\partial/\partial t)$ term can be omitted from (2.1),[2,19] so the sole source of dynamics would then appear to arise from the polymer motion through $\mathbf{R}_{i\alpha}(t)$ and $\sigma_{i\alpha}(t)$. However, it is necessary to still include the random thermal velocity fluctuations $\mathbf{v}^*(\mathbf{r},t)$ in the fluid in order that the pure fluid alone would reach thermal equilibrium as $t \rightarrow \infty$.[2,19] In addition, within the hydrodynamic boundary condition approach customarily used in polymer problems, the $\mathbf{v}^*(\mathbf{r},t)$ drive the Brownian motion of the polymers. Given the neglect of the $\rho_0(\partial/\partial t)$ term, these Gaussian velocity fluctuations have been shown to have the correlation function[2,19]

$$\langle \mathbf{v}_\lambda^*[\mathbf{R}_{j\beta}(t),t]\mathbf{v}_\mu^*[\mathbf{R}_{i\alpha}(t'),t']\rangle_{\text{fluct}} = 2k_{\text{B}}TG_{\lambda\mu}[\mathbf{R}_{j\beta}(t) - \mathbf{R}_{i\alpha}(t)]\delta(t - t') \tag{2.3}$$

where $G_{\lambda,\mu}$ are Cartesian components of the familiar Oseen tensor[18]

$$\mathbf{G}(\mathbf{r} - \mathbf{r}') = [8\pi\eta_0|\mathbf{r} - \mathbf{r}'|]^{-1}[1 + (\mathbf{r} - \mathbf{r}')(\mathbf{r} - \mathbf{r}')|\mathbf{r} - \mathbf{r}'|^{-2}] \tag{2.4}$$

and $k_{\text{B}}T$ is the absolute temperature in energy units.

The simplest hydrodynamic boundary conditions are the no-slip ones

$$\mathbf{v}[\mathbf{R}_{i\alpha}(t),t] = \dot{\mathbf{R}}_{i\alpha} \equiv \frac{\partial}{\partial t}\mathbf{R}_{i\alpha}(t), \qquad \text{all } i,\ \alpha \tag{2.5}$$

The use of (2.5) along with (2.1), (2.2), and the polymer equation (2.8) below enables the friction forces $\{\sigma_{i\alpha}(t)\}$ to be uniquely determined and therefore to be eliminated from the equations of motion.

B. Dynamical Equation for Polymers. The polymer dynamics involves a force balance between the entropic (so-called bead–spring) forces, excluded volume forces, and hydrodynamic forces $-\sigma_{i\alpha}(t)$ acting on bead i of chain α. The entropic force on $i\alpha$ is $\varkappa\sum_m A_{im}R_{m\alpha}(t)$, with $\varkappa = 3k_{\text{B}}T/l^2$, l the Kuhn effective step length, and A_{im} the Rouse matrix[20]

$$\begin{aligned} A_{im} &= 2\delta_{im} - \delta_{i,m+1} - \delta_{i,m-1}, && i,\ m \neq 1 \text{ or } n \\ &= \delta_{im} - \delta_{i,m+1}, && i = 1 \\ &= \delta_{im} - \delta_{i,m-1}, && i = n \end{aligned} \tag{2.6}$$

while the excluded volume force is written as

$$\mathbf{f}_{i\alpha}(t) = -\nabla_{\mathbf{R}_{i\alpha}(t)}\upsilon \sum_{\substack{\beta,j \\ (j\neq i \text{ if } \alpha=b)}} \delta[\mathbf{R}_{i\alpha}(t) - \mathbf{R}_{j\beta}(t)] \tag{2.7}$$

with υ the customary excluded volume.[12,18] Hence, the force balance gives the polymer equation

$$\varkappa\sum_{im}A_{im}\mathbf{R}_{m\alpha}(t) = \mathbf{f}_{i\alpha}(t) - \sigma_{i\alpha}(t) \tag{2.8}$$

Note that the hydrodynamic forces $\sigma_{i\alpha}(t)$ have a random component to them, arising from the fluid velocity fluctuations $\mathbf{v}^*(\mathbf{r},t)$ which are transmitted to the polymer through the simple boundary conditions (2.5).[2] Hence, when (2.8) is determined below, the resultant equation is of a Langevin type, which could, if desired, be converted to an equivalent diffusion equation using the properties (2.3). We retain, however, the Langevin formalism and the multiple-scattering representation generated by it.

C. Macroscopic Fluid Equations. Ultimately, we desire only the configurationally averaged properties where the average is performed over the distribution function for the polymers at some initial or reference time. Since only the zero shear rate limit is treated here, the averaging involves the equilibrium polymer distribution function. Because of the $\{\mathbf{R}_{i\alpha}(t)\}$ on the left side of (2.1), it is clear that $\mathbf{v}(\mathbf{r},t)$ depends on these polymer positions, so this feature is not explicitly written for notational convenience. Designating $\mathbf{u}(\mathbf{r},t) = \langle\mathbf{v}(\mathbf{r},t)\rangle$ as the configurational average over the polymer distribution, the average of (2.1) with the $\rho_0(\partial/\partial t)$ term omitted is then

$$-\eta_0\nabla^2\mathbf{u}(\mathbf{r},t) + \nabla P(\mathbf{r},t) = \langle\sum_{i,\alpha}\delta[\mathbf{r} - \mathbf{R}_{i\alpha}(t)]\sigma_{i\alpha}(t)\rangle \tag{2.9}$$

with the average pressure $\langle P\rangle$ written as P.

The last term on the right in (2.9) is the average friction force density exerted by the polymers on the fluid at $\mathbf{r}$ and t. In the linear viscoelastic domain this friction force density must be proportional to $\mathbf{u}(\mathbf{r},t)$, but the proportionality is, in general, nonlocal in space and time. This may be written as[2]

$$\langle\sum_{i,\alpha}\delta[\mathbf{r} - \mathbf{R}_{i\alpha}(t)]\sigma_{i\alpha}(t)\rangle = \int \mathrm{d}\mathbf{r}' \int_{t_0}^{t}\mathrm{d}t'\,\mathbf{\Sigma}(\mathbf{r} - \mathbf{r}';t - t')\cdot\mathbf{u}(\mathbf{r}',t') + \mathcal{O}(\mathbf{u}^2) \tag{2.10}$$

where $\mathbf{\Sigma}$ is the fluid friction coefficient density tensor, which has been termed the "self-energy" by mathematical analogy with many-body theory.

$\mathbf{\Sigma}$ may be presented in gradient expansion

$$\mathbf{\Sigma}(\mathbf{r} - \mathbf{r}';t - t') = [\delta\eta(t - t')\nabla_{\mathbf{r}}^2 + \mathcal{O}(\nabla_{\mathbf{r}}^4)]\delta(\mathbf{r} - \mathbf{r}') \tag{2.11}$$

so that use of (2.10) and (2.11) in (2.9) and retention of only the $\nabla_{\mathbf{r}}^2$ term yields the macroscopic equations for the averaged fluid

$$-\eta_0\nabla^2\mathbf{u}(\mathbf{r},t) + \nabla P(\mathbf{r},t) - \int_{t_0}^{t}\mathrm{d}t'\,\delta\eta(t - t')\nabla^2\mathbf{u}(\mathbf{r},t') = 0 \tag{2.12}$$

identifying $\delta\eta(t - t')$ as the polymers' contribution to the dynamical viscosity of the averaged solution. Higher terms in the gradient expansion (2.11) introduce effects usually called "microscopic viscosity", reflecting the fact that the solution viscosity does not properly describe dynamics on a more microscopic scale.

It is customary to express the dynamical quantities in terms of frequencies, and this is done by use of Fourier transforms

$$\delta\eta(\omega) = \lim_{\epsilon\rightarrow 0^+}\int_0^\infty \mathrm{d}\tau\,\exp(-i\omega\tau - \epsilon\tau)\delta\eta(\tau) \tag{2.13a}$$

$$\boldsymbol{\Sigma}(\mathbf{r}-\mathbf{r}';\omega) = \lim_{\epsilon\to 0^+}\int_0^\infty \mathrm{d}\tau\, \exp(-i\omega\tau - \epsilon\tau)\boldsymbol{\Sigma}(\mathbf{r}-\mathbf{r}';\tau) \tag{2.13b}$$

The integrals in (2.10) range only over $\tau = t - t' \geq 0$ because the polymers cannot respond *before* the application of a force. Hence, response functions like $\delta\eta$ and $\boldsymbol{\Sigma}$ must be proportional to the step function $\theta(t - t')$. This *causality* condition on $\boldsymbol{\Sigma}$ means that $\boldsymbol{\Sigma}(\mathbf{r} - \mathbf{r}';\omega)$ must be an analytic function of ω in the lower half to plane to ensure that its inverse Fourier transform gives $\boldsymbol{\Sigma}(\mathbf{r} - \mathbf{r}';t - t')$ proportional to $\theta(t - t')$.[7] The $\epsilon \to 0^+$ limiting procedure ensures that real frequencies are approached from the lower half plane. It also defines how functions of the singular $\mathbf{A}$ matrix (2.6) are to be handled. The neglect of this subtle limiting process, often unnecessary in general problems of linear response, led to numerical errors in the early multiple-scattering calculations. With proper treatment of these limits[7] the multiple-scattering method has been used to generate an exact correlation function representation for the intrinsic viscosity of a Gaussian chain. When the popular preaveraging approximation is introduced, this exact expression becomes identical with that provided by the Rouse–Zimm theory.[18,21] The multiple-scattering theory, however, can also treat the concentration dependence.[1-8] We seek here to obtain the generalization of these previous formal results to polymers with excluded volume forces.

D. Method for Determination of $\boldsymbol{\Sigma}$. Equations for (2.1), (2.2), (2.5), and (2.7) must be solved simultaneously to determine the fluid velocity field $\mathbf{v}(\mathbf{r},t)$ as a function of the $\{\mathbf{R}_{\alpha i}\}$ and thereby yield $\mathbf{u}(\mathbf{r},t)$ as the average. The multiple-scattering method gives $\mathbf{u}(\mathbf{r},t)$ as a series involving the Oseen tensor $\mathbf{G}$ of (2.4). (See section III.) If (2.9) with (2.10) is solved in a similar expansion, we obtain

$$\mathbf{u}(\mathbf{r},t) = \mathbf{v}_0^*(\mathbf{r},t) + \int\int \mathrm{d}\mathbf{r}'\, \mathrm{d}\mathbf{r}'' \int_{t_0}^{t} \mathrm{d}t'\, \mathbf{G}(\mathbf{r}-\mathbf{r}')\cdot \boldsymbol{\Sigma}(\mathbf{r}-\mathbf{r}'';t-t')\cdot\mathbf{v}_0^*(\mathbf{r}'',t') + \int \mathbf{G}\cdot\boldsymbol{\Sigma}\cdot\mathbf{G}\cdot\boldsymbol{\Sigma}\cdot\mathbf{v}_0^* + \ldots \tag{2.14}$$

where higher terms in the series are written in symbolic notation with dummy variables and integrations implicit. $\mathbf{v}_0^*$ is the sum of the imposed velocity field $\mathbf{v}_0(\mathbf{r},t)$ and the random velocity fluctuations $\mathbf{v}^*(\mathbf{r},t)$

$$\mathbf{v}_0^*(\mathbf{r},t) = \mathbf{v}_0(\mathbf{r},t) + \mathbf{v}^*(\mathbf{r},t) \tag{2.15}$$

$\boldsymbol{\Sigma}$ can be obtained by comparing (2.14) with the multiple-scattering solutions in section III, and then expressions for the polymer viscosity may readily be extracted. The related effective medium theory[3,5,6,8] takes the hydrodynamic disturbances to be propagated through the averaged polymer solution as described by the effective concentration-dependent hydrodynamic interactions $\mathbf{G}(\mathbf{r} - \mathbf{r}';c)$ rather than the pure fluid Oseen tensor. The expansion procedure is more involved, but the basic techniques are related.

III. Multiple-Scattering Expansion

A. Derivation of Multiple-Scattering Solution for the Fluid Velocity. The formal solution of (2.1) with (2.2) and $\rho_0(\partial/\partial t)$ omitted is readily solved by using the Oseen tensor $\mathbf{G}$ of (2.4)

$$\mathbf{v}(\mathbf{r},t) = \mathbf{v}_0^*(\mathbf{r},t) + \sum_{i,\alpha} \mathbf{G}[\mathbf{r} - \mathbf{R}_{i\alpha}(t)]\cdot\boldsymbol{\sigma}_{i\alpha}(t) \tag{3.1}$$

The hydrodynamic boundary conditions (2.5) are applied to (3.1) to give

$$\dot{\mathbf{R}}_{i\alpha}(t) = \mathbf{v}_0^*[\mathbf{R}_{i\alpha}(t),t] + \sum_{\beta,j} \mathbf{G}[\mathbf{R}_{i\alpha}(t) - \mathbf{R}_{\beta j}(t)]\cdot\boldsymbol{\sigma}_{j\beta}(t) \tag{3.2}$$

Multiplying the polymer equation (2.8) for $j\beta$ by $\sum_{\beta j}\mathbf{G}[\mathbf{R}_{i\alpha}(t) - \mathbf{R}_{j\beta}(t)]$ yields

$$\sum_{\beta,j} \mathbf{G}[\mathbf{R}_{i\alpha}(t) - \mathbf{R}_{j\beta}(t)]\cdot\boldsymbol{\sigma}_{j\beta}(t) = -\sum_{\beta,jm} \mathbf{G}[\mathbf{R}_{i\alpha}(t) - \mathbf{R}_{j\beta}(t)]\varkappa A_{jm}\cdot \mathbf{R}_{m\beta}(t) + \sum_{\beta,j} \mathbf{G}[\mathbf{R}_{i\alpha}(t) - \mathbf{R}_{j\beta}(t)]\cdot\mathbf{f}_{j\beta}(t) \tag{3.3}$$

Equations 3.2 and 3.3 can be combined to eliminate the terms in $\mathbf{G}\cdot\boldsymbol{\sigma}$. It is then convenient, following the approach without excluded volume, to separate the contributions $\beta = \alpha$ from $\beta \neq \alpha$, leaving

$$\dot{\mathbf{R}}_{i\alpha}(t) + \sum_{jm} \mathbf{G}[\mathbf{R}_{i\alpha}(t) - \mathbf{R}_{j\alpha}(t)]\varkappa A_{jm}\cdot\mathbf{R}_{m\alpha}(t) - \sum_{j} \mathbf{G}[\mathbf{R}_{i\alpha}(t) - \mathbf{R}_{j\alpha}(t)]\cdot\mathbf{f}_{j\alpha}(t) = \mathbf{v}_0^*[\mathbf{R}_{i\alpha}(t),t] - \sum_{\beta\neq\alpha,j} \mathbf{G}[\mathbf{R}_{i\alpha}(t) - \mathbf{R}_{j\beta}(t)]\cdot[\sum_{m}\varkappa A_{jm}\boldsymbol{R}_{m\beta}(t) - \mathbf{f}_{j\beta}(t)] \tag{3.4}$$

We now require a formal solution of the single-chain form of (3.4) where terms in $\beta \neq \alpha$ are absent on the left-hand side. This a highly nonlinear equation in $\{\mathbf{R}_{i\alpha}(t)\}$, but a formal solution may be obtained by introducing the identity

$$\mathbf{f}_{j\alpha}(t) \equiv -\upsilon\sum_{i} \nabla_{\mathbf{R}_{j\alpha}(t)}\delta[\mathbf{R}_{j\alpha}(t) - \mathbf{R}_{i\alpha}(t)]\cdot\nabla_{\mathbf{R}_{i\alpha}(t)}\mathbf{R}_{i\alpha}(t) - \upsilon \sum_{\beta\neq\alpha,i} \nabla_{\mathbf{R}_{j\alpha}(t)}\delta[\mathbf{R}_{j\alpha}(t) - \mathbf{R}_{i\beta}(t)] \equiv \sum_{i} h_{\alpha,ji}(t)\mathbf{R}_{i\alpha}(t) + \delta\mathbf{f}_{j\alpha}(t) \tag{3.5}$$

Here, $h\mathbf{R}$ includes the intrachain excluded volume force, while $\delta\mathbf{f}$ is the interchain paart. Introduct the notation

$$\Delta_{\alpha,ij}(t) \equiv \varkappa A_{ij} - h_{\alpha,ij} \tag{3.6}$$

so (3.5) and (3.6) transform (3.4) into

$$\dot{\mathbf{R}}_{i\alpha}(t) + \sum_{jm} \mathbf{G}[\mathbf{R}_{i\alpha}(t) - \mathbf{R}_{j\alpha}(t)]\Delta_{\alpha,jm}(t)\cdot\mathbf{R}_{m\alpha}(t) = \mathbf{v}_0^*[\mathbf{R}_{i\alpha}(t),t] - \sum_{\beta\neq\alpha,jm} \mathbf{G}[\mathbf{R}_{i\alpha}(t) - \mathbf{R}_{j\beta}(t)]\Delta_{\beta,jm}(t)\cdot\mathbf{R}_{m\beta}(t) - \sum_{\beta j} \mathbf{G}[\mathbf{R}_{i\alpha}(t) - \mathbf{R}_{j\beta}(t)]\cdot\delta\mathbf{f}_{j\beta}(t) \tag{3.7}$$

The formal solution to (3.7) can be expressed in terms of the single-chain response

$$\sum_{p}\left\{\frac{\partial}{\partial t}\mathbf{1}\delta_{jp} + \sum_{i} \mathbf{G}[\mathbf{R}_{j\alpha}(t) - \mathbf{R}_{i\alpha}(t)]\Delta_{\alpha,ip}\right\}\cdot\mathbf{g}_{pm}(t,t') = \delta_{jm}\mathbf{1}\delta(t - t') \tag{3.8}$$

as the nonlinear integral equation

$$\mathbf{R}_{i\alpha}(t) = \int \mathrm{d}t' \sum_{j} \mathbf{g}_{\alpha,ij}(t,t')\cdot\{\mathbf{v}_0^*[\mathbf{R}_{j\alpha}(t'),t'] - \sum_{\substack{\beta\neq\alpha\\ mp}} \mathbf{G}[\mathbf{R}_{j\alpha}(t') - \mathbf{R}_{m\beta}(t')]\cdot\Delta_{\beta,mp}\mathbf{R}_{p\beta}(t') + \sum_{\beta m} \mathbf{G}[\mathbf{R}_{j\alpha}(t') - \mathbf{R}_{m\beta}(t')]\cdot\delta\mathbf{f}_{m\beta}(t')\} \tag{3.9}$$

Equation 3.9 can be iterated indefinitely for $\mathbf{R}_{i\alpha}(t)$ in the linear factor involving the second term in curly brackets on the right of (3.9). Multiplying this infinite series for $\mathbf{R}_{m\alpha}(t)$ by $\varkappa\sum_m A_{im}$ and using (2.8) yields a multiple-scattering expansion for $\sigma_{i\alpha}(t)$, which may then be inserted into (3.1) to provide the multiple-scattering solution for the instantaneous velocity field $\mathbf{v}(\mathbf{r},t)$ as a function of the chain dynamics $\{\mathbf{R}_{i\alpha}(t)\}$

$$\mathbf{v}(\mathbf{r},t) = \int\int \mathbf{dr}'\, \mathrm{d}t'\, \hat{\mathbf{L}}(\mathbf{r},\mathbf{r}';t,t'|[\mathbf{R}_{\alpha i}(\tau)])\cdot\mathbf{v}_0^*(\mathbf{r}',t') + \sum_{z\omega}\int \mathrm{d}t'\, \hat{\mathbf{G}}(\mathbf{r},\mathbf{R}_{z\omega}(t');t,t'|[\mathbf{R}_{i\alpha}(\tau)])\cdot\delta\mathbf{f}_{z\omega}(t') \tag{3.10}$$

$$\hat{L}(\mathbf{r},\mathbf{r}';t,t'|[\mathbf{R}_{i\alpha}(\tau)]) = \delta(\mathbf{r}-\mathbf{r}')\delta(t-t')\mathbf{1} - \sum_{\alpha}\int \mathrm{d}\mathbf{r}_1\, \mathbf{G}(\mathbf{r}-\mathbf{r}_1)\cdot\mathbf{T}_\alpha(\mathbf{r}_1,\mathbf{r}';t,t'|[\mathbf{R}_{i\alpha}(\tau)]) + \sum_{\alpha}\sum_{\beta\neq\alpha} \mathbf{G}\cdot\mathbf{T}_\alpha\cdot\mathbf{G}\cdot\mathbf{T}_\beta - \sum_{\alpha}\sum_{\beta\neq\alpha}\sum_{\gamma\neq\beta} \mathbf{G}\cdot\mathbf{T}_\alpha\cdot\mathbf{G}\cdot\mathbf{T}_\beta\cdot\mathbf{G}\cdot\mathbf{T}_\gamma + \ldots \tag{3.11}$$

$$\mathbf{T}_\alpha(\mathbf{r},\mathbf{r}';t,t'|[\mathbf{R}_{i\alpha}(\tau)]) = \sum_{ijm}\delta[\mathbf{r} - \mathbf{R}_{i\alpha}(t)]\Delta_{\alpha,ij}\mathbf{g}_{jm}(t,t')\delta[\mathbf{r}' - \mathbf{R}_{m\alpha}(t')] \quad (3.12)$$

$$\hat{G}(\mathbf{r},\mathbf{r}';t,t'|[\mathbf{R}_{i\alpha}(\tau)]) = \int \mathrm{d}\mathbf{r}''\ \hat{\mathbf{L}}(\mathbf{r},\mathbf{r}'';t,t'|[\mathbf{R}_{i\alpha}(\tau)])\cdot\mathbf{G}(\mathbf{r}'' - \mathbf{r}') \quad (3.13)$$

In these equations $\hat{\mathbf{G}}$ is the dynamical screened Oseen tensor for the whole polymer solution, $\mathbf{T}_\alpha\cdot\mathbf{v}_0{}^*$ describes the perturbed velocity field for a single chain α in solution, and symbolic notation is used in (3.12) with integration over all intermediate space and time variables.

B. Average Fluid Velocity. The fluid velocity in (3.10) depends on the stochastic trajectories of all the chain segments in solution, and it is therefore a rather complicated beast. Fortunately, we desire the average of (3.10) over all chain conformations at some initial time t_0 as well as over the random velocity fluctuations in the fluid. Averaging $\mathbf{v}$ over velocity fluctuations defines $\bar{\mathbf{v}}$. We approximate the former average of the right-hand side of (3.10) by the replacement

$$\bar{\mathbf{v}}_0{}^* = \mathbf{v}_0 \quad (3.14)$$

while the latter average is expressed by brackets $\langle ...\rangle$, so $\langle \mathbf{v}\rangle \equiv \mathbf{u}$. Equation 3.10 implies that $\mathbf{u}$ depends formally on the interparticle excluded volume forces $\delta\mathbf{f}_{z\omega}(t')$, but these terms can be shown to vanish upon configurational averaging (see below).

Introduce the distribution P by

$$\langle B(\{\mathbf{R}_{i\alpha}\})\rangle = \int \mathrm{d}\{\mathbf{R}_{i\alpha}\}\ B(\{\mathbf{R}_{i\alpha}\})P(\{\mathbf{R}_{i\alpha}\}) \quad (3.15)$$

The configuration average of the $\delta\mathbf{f}$ term in (3.10) utilizes the equilibrium distribution function $P(\{\mathbf{R}_{i\alpha}\})$ at time t' since we ultimately consider the limit of infinitesimal $\mathbf{v}_0$. The series (3.11) implies that all these $\delta\mathbf{f}$ terms in (3.10) have the right-most factors of

$$\sum_{z\omega}\langle ...\mathbf{G}[\mathbf{r} - \mathbf{R}_{z\omega}(t')]\cdot\delta\mathbf{f}_{z\omega}(t')\rangle = -\upsilon\langle ...\sum_{z\omega}\sum_{j,\gamma\neq\omega}\mathbf{G}[\mathbf{r} - \mathbf{R}_{z\omega}(t')]\cdot\nabla_{\mathbf{R}_{z\omega}(t')}\delta[\mathbf{R}_{z\omega}(t') - \mathbf{R}_{j\gamma}(t')]\rangle \quad (3.16a)$$

A particular pair of segments $z\omega$ and γj appears in each of the two summations on the right side of (3.16a), so separating the contribution from one such pair gives

$$-\upsilon\langle ...\mathbf{G}[\mathbf{r} - \mathbf{R}_{z\omega}(t')]\cdot[\nabla_{\mathbf{R}_{z\omega}(t')} + \nabla_{\mathbf{R}_{j\gamma}(t')}]\delta[\mathbf{R}_{z\omega}(t') - \mathbf{R}_{j\gamma}(t')]\rangle \quad (3.16b)$$

where the presence of the δ function is used to convert $\mathbf{R}_{\gamma j}(t')$ in one of the $\mathbf{G}$'s into a $\mathbf{R}_{z\omega}(t')$. Introduction of (3.15) for the averaging followed by partial integration yields

$$-\upsilon\int \mathrm{d}\{\mathbf{R}_{i\alpha}(t')\}...\mathbf{G}[\mathbf{r} - \mathbf{R}_{z\omega}(t')]\cdot\{[\nabla_{\mathbf{R}_{z\omega}(t')} + \nabla_{\mathbf{R}_{j\gamma}(t')}]\delta[\mathbf{R}_{z\omega}(t') - \mathbf{R}_{j\gamma}(t')]P[\mathbf{R}_{j\gamma}(t'),\mathbf{R}_{z\omega}(t'),...] = +\upsilon\int \mathrm{d}\{\mathbf{R}_{i\alpha}(t')\}...\mathbf{G}[\mathbf{r} - \mathbf{R}_{z\omega}(t')]\cdot\{[\nabla_{\mathbf{R}_{z\omega}(t')} + \nabla_{\mathbf{R}_{j\gamma}(t')}]P[\mathbf{R}_{j\gamma}(t'),\mathbf{R}_{z\omega}(t'),...]\}_{\mathbf{R}_{z\omega}(t')=\mathbf{R}_{j\gamma}(t')} \quad (3.16c)$$

where boundary terms in the partial integration vanish since $P \rightarrow 0$ as $R_{z\omega}(t') \rightarrow \infty$ and the $\nabla\cdot\mathbf{G}^{\mathrm{T}}$ contributions vanish because of fluid incompressibility and the fact that $\mathbf{G}$ equals its transpose $\mathbf{G}^{\mathrm{T}}$. The last two factors in (3.16c) provide a total derivative, so (3.16c) equals

$$\upsilon\int \mathrm{d}\{\mathbf{R}_{i\alpha}(t')\}/\mathrm{d}\mathbf{R}_{j\gamma}(t')...\mathbf{G}[\mathbf{r} - \mathbf{R}_{z\omega}(t')]\cdot\nabla_{\mathbf{R}_{z\omega}(t')}P[\mathbf{R}_{z\omega}(t'),\mathbf{R}_{z\omega}(t'),...] \quad (3.16d)$$

which vanishes since partial integration again yields $\nabla\cdot\mathbf{G}^{\mathrm{T}} = 0$ and the boundary terms are again zero. Consequently, eq 3.16 implies that the configurational average of all $\delta\mathbf{f}$ terms in (3.10) vanish, leaving the more compact result

$$\bar{\mathbf{u}}(\mathbf{r},t) = \mathbf{v}_0(\mathbf{r},t) - \sum_\alpha \mathbf{G}\cdot\langle\mathbf{T}_\alpha\rangle\cdot\mathbf{v}_0 + \sum_\alpha\sum_{\beta\neq\alpha}\mathbf{G}\cdot\langle\mathbf{T}_\alpha\cdot\mathbf{G}\cdot\mathbf{T}_\beta\rangle\cdot\mathbf{v}_0 + ... \quad (3.17)$$

in symbolic notation.

C. Dynamical Intrinsic Viscosity. Note that (3.17) has the same multiple-scattering structure as obtained for polymer chains in "Θ" solutions, where $\mathbf{f} = 0$.[2,7,8] The only difference occurs through the excluded volume contributions to the $\mathbf{T}_\alpha$ of (3.12). Hence, our previous results[1-8] can immediately be used for expressing $\mathbf{\Sigma}$ of (2.10) in terms of $\mathbf{T}_\alpha$, for extracting the concentration-dependent dynamical viscosity, and for converting (3.17) to effective medium type equations. Details are quoted as necessary. For instance, the dynamical intrinsic viscosity emerges as the coefficient of $\mathbf{1}k^2 - \mathbf{kk}$ in the $\mathbf{k}$ expansion of

$$\eta_0{}^{-1}\Sigma_{\mu\nu}^{(1)}(\mathbf{k},\omega) = \frac{N}{\eta_0 V}\lim_{\epsilon\rightarrow 0^+}\int_0^\infty \mathrm{d}\tau\ \exp(-i\omega\tau - \epsilon\tau)\sum_{ijm}\langle\exp[i\mathbf{k}\cdot\mathbf{r}_i(t)]\Delta_{ij}(t)g_{jm,\mu\nu}(t,t'|\{\mathbf{r}_p(\tau)\})\ \exp[-i\mathbf{k}\cdot\mathbf{r}_m(t')]\rangle \quad (3.18)$$

where $\mathbf{r}_i(t)$ designates the position of segment i at time t with respect to the chain center of mass, and μ and ν label Cartesian components of tensors. This formal result could form the basis of numerical simulations because it is an *exact* correlation function form.

The quantity $\mathbf{g}(t,t')$ in (3.9) and (3.18) poses a central impediment to numerical solutions. [Note that the $\mathbf{r}_p(\tau)$ can be written in terms of $\mathbf{g}(\tau,t_0)$.] A formally exact solution for $\mathbf{g}$ is given as $(t > t_0)$

$$\mathbf{g}(t,t_0) = T\exp\left[-\int_{t_0}^{t}\mathrm{d}\tau\ \mathbf{K}(\tau)\Delta(\tau)\right] \quad (3.19)$$

$$\mathbf{K}_{ij}(t) \equiv \mathbf{G}[\mathbf{R}_{i\alpha}(t) - \mathbf{R}_{j\alpha}(t)] \quad (3.19a)$$

where the time-ordering operator T acts on all terms to its right in the expansion of the exponential by

$$\begin{aligned} T[A(t_1)B(t_2)] &= A(t_1)B(t_2) \qquad t_1 > t_2 \\ &= B(t_2)A(t_1) \qquad t_1 < t_2 \end{aligned} \quad (3.20)$$

In the renormalization group method,[15-17] $\mathbf{K}$ and $\mathbf{f}$ are considered to be first-order quantities, so a perturbational expansion of $\mathbf{g}$ based on (3.19) is possible. However, $\mathbf{K}\Delta$ plays the role of a relaxation time matrix (nondiagonal), so it is sensible to utilize perturbation expansions directly in the exponential of (3.19). These types of time-ordered expansions are well understood elsewhere, and they eliminate the difficulties with secular terms arising from a straightforward expansion of (3.19) in powers of $\mathbf{K}\Delta$. Hence, (3.18) and (3.19) can be utilized as the basis for a renormalization group calculation of the single-chain dynamical viscosity. The Kirkwood–Riseman approach of Oono and Kohmoto[17] only yields static quantities. Likewise, the concentration-dependent viscosity and friction coefficients may be obtained from previous formal multiple-scattering results by the simple replacement of $\varkappa A$ by Δ everywhere. Thus, the concentration dependence is also amenable to these techniques.

The treatment of (3.19) is expected to be very difficult, so it is natural to introduce some suitable approximation schemes. A sensible one involves the identity

$$\mathbf{K}(\tau)\Delta(\tau) \equiv \langle\mathbf{K}(\tau)\Delta(\tau)\rangle + \{\mathbf{K}(\tau)\Delta(\tau) - \langle\mathbf{K}(\tau)\Delta(\tau)\rangle\} \quad (3.21)$$

where the average is over all chain conformations as in (3.18). The first term $\langle \mathbf{K}\Delta \rangle$ on the right-hand side of (3.21) is just an equilibrium average and may be evaluated by equilibrium methods, e.g., by the renormalization group.[12-14] The remainder is a perturbation to be expanded. Rather than pursuing this full perturbation expansion, we consider here the approximation of retaining only the leading term in $\langle \mathbf{K}\Delta \rangle$, the preaveraging approximation.

D. Dynamical Intrinsic Viscosity in the Preaveraging Approximation. Using $P(\{\mathbf{r}_i\})$, the internal segment distribution function (3.15), $\langle \mathbf{K}\Delta \rangle$ is then given by

$$\langle \mathbf{K}\Delta \rangle = \int \mathrm{d}\{\mathbf{r}_i\} \sum_j \mathbf{G}(\mathbf{r}_i - \mathbf{r}_j)[\varkappa A_{jm} - h_{jm}] P(\{\mathbf{r}_i\}) = \int \mathrm{d}\{\mathbf{r}_i\} \sum_j \mathbf{G}(\mathbf{r}_i - \mathbf{r}_j)[\varkappa A_{jm} + \upsilon \nabla_{\mathbf{r}_j} \cdot \nabla_{\mathbf{r}_m} \delta(\mathbf{r}_j - \mathbf{r}_m)] P(\{\mathbf{r}_i\}) \tag{3.22}$$

where the second equality follows from partial integration and the condition that $P(\{\mathbf{r}_i\}) \rightarrow 0$ as any $\mathbf{r}_i \rightarrow \infty$. The further simple approximation of separating the averages

$$\langle \mathbf{K}\Delta \rangle \simeq \langle \mathbf{K} \rangle \langle \Delta \rangle \tag{3.23}$$

yields the separate quantities

$$\langle \mathbf{K}_{ij} \rangle = \mathbf{1} \zeta^{-1} H_{ij}^{\upsilon} \tag{3.24a}$$

$$\langle \Delta_{jm} \rangle = \varkappa A_{jm} + \upsilon \langle \nabla_{\mathbf{r}_j} \cdot \nabla_{\mathbf{r}_m} \delta(\mathbf{r}_i - \mathbf{r}_m) \rangle \equiv F_{jm}^{\upsilon} \tag{3.24b}$$

with H_{ij}^{υ} the Zimm matrix appropriate to a polymer with excluded volume, and the second term in F_{jm}^{υ} of (3.24b) is clearly the equilibrium average force constant for segments i and j as contributed by the excluded volume interaction. (It is the thermal average of the Hessian of the excluded volume potential of mean force.) A nonuniformly scaled force constant matrix like F_{jm}^{υ} is present in phenomenological and scaling motivated treatments of the concentration dependence of the viscoelastic properties of polymer solutions.[4,5] The H_{ij}^{υ} matrix has recently been calculated by the renormalization group methods for linear and star polymers with excluded volume as a function of the strength of the excluded volume interaction.[22] The more precise preaveraging approach follows (3.21) and can be treated with approximations to $P(\{\mathbf{r}_i\})$ for chains with excluded volume.

Muthukumar and Edwards[11] have studied the concentration dependence of the viscosity of polymer solutions with excluded volume by the use of an approximate stochastic linearization. Their theory for the single chain effectively uses the separation (3.23) and an approximate distribution function $P_a(\{\mathbf{r}_i\})$ in which the individual Rouse modes ζ_p have their mean square values $\langle |\zeta_p|^2 \rangle$ as evaluated with P_a scaled by $\alpha(p)$ to provide a nonuniform scaling model. The value of $\langle \Delta \rangle$ and these $\alpha(p)$ are then solved self-consistently. This basic approach is also used at nonzero concentrations, where the $\alpha(p)$ become functions of concentration. There is, however, a serious further assumption in their treatment which involves a static, $t = t'$ approximation to the correlation function $\langle \exp\{i\mathbf{k} \cdot [\mathbf{r}_i(t) - \mathbf{r}_j(t')]\} \rangle$ of (3.18) and related terms in the concentration-dependent effective medium version thereof with $\mathbf{K}$ replaced by the hydrodynamically screened $\hat{\mathbf{K}}$. This approximation is now known[5,7] to produce errors of factors of 2 in the calculated intrinsic viscosity as well as other errors in the dynamical viscosity, so it should not be utilized for quantitative purposes. The static approximation had been introduced earlier by Freed and Edwards[1,2] to study hydrodynamic screening in polymer solutions, and it is adequate for these qualitative purposes. It should be noted that we have shown that the spatial Fourier transform of (2.13b) $\mathbf{\Sigma}(\mathbf{k},\omega)$ has the exact dependence of $\mathbf{\Sigma}(0,0) \equiv 0$ for flowing polymers; $\mathbf{\Sigma}(0,0)$ need not vanish with impeding flow entanglements.[7] However, Freed and Edwards *effectively* use the condition that $\mathbf{\Sigma}(\mathbf{k},0)$ is constant for $\mathbf{k}$ comparable to a chain size although they incorrectly present it as $\mathbf{\Sigma}(0,0) \neq 0$.

Given the approximations (3.21) and (3.23), the general expression (3.18) can be reduced to the preaveraging approximation

$$\eta_0^{-1} \mathbf{\Sigma}^{(1)}(\mathbf{k},\omega) \simeq \frac{N}{\eta_0 \upsilon} \mathbf{1} \lim_{\epsilon \rightarrow 0^+} \int_0^{\infty} \mathrm{d}\tau \exp(-i\omega\tau - \epsilon\tau) \sum_{ijm} \langle \exp\{i\mathbf{k} \cdot [\mathbf{r}_i(t) - \mathbf{r}_j(t')]\} \rangle F_{ij}^{\upsilon} [\exp(-\zeta^{-1} \mathbf{H}^{\upsilon} \mathbf{F}^{\upsilon} \tau)]_{jm} \tag{3.25}$$

where in this approximation the use of the averaged $\mathbf{g}_{jm}$ removes it from the conformational average, and the remaining average of the exponential factor and Δ_{ij} is broken into the product of the separate averages in the same spirit as (3.23).

In order to extract the viscosity as the coefficient of k^2 in (3.25), it is necessary to prove a fundamental theorem which is trivially obeyed in the cause of Gaussian chains. The condition

$$\sum_j A_{jm} = \sum_m A_{jm} \equiv 0 \tag{3.26}$$

has been utilized[7,8] to further simplify the Gaussian chain analogue of (3.25) and convert it to a form identical with that emerging from the Rouse–Zimm[18,21] theory. We now show that the matrix $\mathbf{F}^{\upsilon}$ has this same important property. Actually, the arguments are more general than for the specific case of a δ-function potential, so we utilize a general interaction for now instead of (3.24b). The F_{jm}^{υ} is

$$F_{jm}^{\upsilon} = \varkappa A_{jm} - \langle \nabla_{\mathbf{r}_j} \cdot \nabla_{\mathbf{r}_m} V(\mathbf{r}_i - \mathbf{r}_m) \rangle = \langle \nabla_{\mathbf{r}_j} \cdot \nabla_{\mathbf{r}_m} U \rangle \tag{3.27}$$

with U the total potential energy (actually potential of mean force), including both entropic and excluded volume portions. The total potential energy is pairwise additive of the general form

$$U = \tfrac{1}{2} \sum_{j \neq m} U(\mathbf{r}_j - \mathbf{r}_m) \tag{3.28}$$

so the force on j is given by

$$\mathbf{F}_j = -\nabla_{\mathbf{r}_j} [\tfrac{1}{2} \sum_{j \neq m} U(\mathbf{r}_j - \mathbf{r}_m)] = \sum_m \nabla_{\mathbf{r}_m} U(\mathbf{r}_j - \mathbf{r}_m) \tag{3.29}$$

The divergence of $\mathbf{F}_j$ is obtained as

$$\nabla_{\mathbf{r}_j} \cdot \mathbf{F}_j \tag{3.30}$$

Hence, summing (3.27) over m and comparing with (3.30) implies

$$\sum_m F_{jm}^{\upsilon} = \langle \nabla_{\mathbf{r}_j} \cdot \mathbf{F}_j \rangle = -\int \mathrm{d}\{\mathbf{r}_i\} \left[\nabla_{\mathbf{r}_j}^{2} U \right] P(\{\mathbf{r}_i\}) \tag{3.31}$$

Since $P \propto \exp[-\beta U]$, (3.31) can be written as

$$\sum_m F_{jm}^{\upsilon} = \frac{1}{\beta} \int \mathrm{d}\{\mathbf{r}_i\} \nabla_{\mathbf{r}_j} \cdot [\nabla_{\mathbf{r}_j} P(\{\mathbf{r}_i\})] = 0 \tag{3.32}$$

where partial integration with respect to $\mathbf{r}_j$ leads to the last equality. Likewise, it readily follows that

$$\sum_j F_{jm}^{\upsilon} = \sum_m F_{jm}^{\upsilon} = 0 \tag{3.33}$$

Given the condition (3.33), then (3.25) is of the same mathematical structure as the case of Gaussian chains treated by Freed and Perico,[7] where we have the replacements $\zeta^{-1}\mathbf{H} \rightarrow \zeta^{-1}\mathbf{H}^{\upsilon}$ and $\varkappa\mathbf{A} \rightarrow \mathbf{F}^{\upsilon}$. Hence, we may quote their results with these replacements. Equation 3.33 implies that $\mathbf{\Sigma}^{(1)}(0,0) \equiv 0$ as noted above and also that to order k^2 in the expansion of the exponential, only the term involving $\langle \mathbf{r}(t)\cdot\mathbf{r}_j(t')\rangle$ contributes.

We now introduce the transformation $\mathbf{Q}$, diagonalizing the matrix $\mathbf{H}^\upsilon\mathbf{F}^\upsilon$ as well as the matrices $\mathbf{M}^\upsilon$ and $\mathbf{N}^\upsilon$ with diagonal elements $\mu_a{}^\upsilon$ and $\nu_a{}^\upsilon$, respectively

$$\mathbf{Q}^{\mathrm{T}}\mathbf{F}^\upsilon\mathbf{Q} = \mathbf{M}^\upsilon \tag{3.34a}$$

$$\mathrm{Q}^{-1}\mathbf{H}^\upsilon(\mathbf{Q}^{-1})^{\mathrm{T}} = \mathbf{N}^\upsilon \tag{3.34b}$$

This enables us to write, for instance

$$[\exp(-\zeta^{-1}\mathbf{H}^\upsilon\mathbf{F}^\upsilon\tau)]_{jm} = \sum_a \mathrm{Q}_{ja} \exp(-\zeta^{-1}\mu_a{}^\upsilon\nu_a{}^\upsilon\tau)(\mathrm{Q}^{-1})_{am} \tag{3.35}$$

The condition (3.33) implies (as with the $\mathbf{A}$ matrix)

$$\mu_0{}^\upsilon = 0 \tag{3.34c}$$

The (3.25) may be expanded in powers of $\mathbf{k}$ with the dynamical viscosity obtained as the coefficient of k^2. Following identically the analysis of Freed and Perico,[7] we obtain

$$[\eta(\omega)] = \frac{k_{\mathrm{B}}TN_{\mathrm{A}}}{M_{\mathrm{A}}n\eta_0}\sum_a \frac{\tau_a{}^\upsilon}{1 + i\omega\tau_a{}^\upsilon} \tag{3.36}$$

where $k_{\mathrm{B}}T$ is the absolute temperature in energy units, N_{A} is Avogadro's number, M_{A} is the monomer molecular weight, n is the number of monomers in the chain, and the viscoelastic relaxation times are

$$\tau_a{}^\upsilon = (2\zeta^{-1}\mu_a{}^\upsilon\nu_a{}^\upsilon)^{-1} \tag{3.37}$$

Equation 3.36 is just of the standard Rouse–Zimm form, except that the effects of excluded volume are fully included within the preaveraging approximation. Some parts of this approximation may readily be lifted by, for instance, not breaking the average in (3.23). Further generalizations involve retention of the correction terms in brackets in (3.21) and treating them by perturbation theory. This is in the same spirit as perturbational treatments of corrections to the preaveraging approximation for a Gaussian chain.[18] However, the presence of excluded volume greatly complicates the computations. Systematic approaches to the description of excluded volume such as renormalization group methods may be employed to our dynamical problems at various levels of sophistication. The most general form approaches the full dynamical correlation function (3.25), while the least considers (3.36). The latter then involves the evaluation of the excluded volume effects on the matrices $\mathbf{H}^\upsilon$ and $\mathbf{F}^\upsilon$. We have already calculated $\mathbf{H}^\upsilon$ to first order in ϵ, as a function of the strength of the excluded volume interaction, for both star and linear polymers,[22] and $\mathbf{H}^\upsilon$ can likewise be determined. We plan to use such calculations in studying excluded volume effects on $[\eta(\omega)]$ in linear and star polymers.

E. Friction Coefficients. The inclusion of excluded volume contributions to friction coefficients proceeds in a similar vein. Cooperative friction coefficients are obtained by appending an external force $\mathbf{f}_{i\alpha}{}^{\mathrm{ext}}(t)$ to eq 3.8.[8] The final averaged velocity field in the fluid is then of the form (3.10) with $\delta\mathbf{f}_{z\omega}(t')$ replaced by $\delta\mathbf{f}_{z\omega}(t') + \mathbf{f}_{z\omega}{}^{\mathrm{ext}}(t')$, and all previous results[8] can be utilized. Similar arguments apply to the self-friction coefficients.[8] Basically, in both of these cases we merely make the replacement of $\varkappa\mu_a \rightarrow \mu_a{}^\upsilon$, $\nu_a \rightarrow \nu_a{}^\upsilon$ within the simplest preaveraging approximation. Since the details follow along the same lines as given above for the intrinsic viscosity, they are not reproduced here.

F. Concentration Dependences. In addition, the description of the concentration dependence of the viscosity, friction coefficients, and mode relaxation times parallels that given for the multiple-scattering theory with the replacement of $\varkappa\mathbf{A}$ by $\mathbf{F}^\upsilon$ and $\mathbf{H}$ by $\mathbf{H}^\upsilon$, etc. Even the effective medium formulation of these concentration dependences can likewise be accomplished. The evaluation of these expressions involves the consideration of the bead–bead dynamical correlation function.[7,8]

$$F^{ij}(\mathbf{k},\tau) = \langle \exp\{i\mathbf{k}\cdot[\mathbf{r}_i(\tau) - \mathbf{r}_j(0)]\}\rangle \tag{3.38}$$

and this is a rather complicated task for polymers with excluded volume. We have used preaveraging-type approximations[7,8] like (3.23) to (3.38) for Gaussian chains at infinite dilution. Then (3.38) involves an exponential of a sum over normal mode contributions, a form which is rather unwieldly to handle computationally.[23,24] Nevertheless, a similar approach, already implicit in obtaining (3.36), is a sensible start in treatment excluded volume effects. It will be of interest to use renormalization group type methods to compare the preaveraged form of (3.38) with a complete dynamical treatment even given limitations of the ϵ-expansion approach.

IV. Discussion

We have generalized the multiple-scattering theory of the concentration dependence of viscoelastic properties, friction coefficients, and relaxation times to incorporate excluded volume effects within the formal structure of the theory. It is explicitly demonstrated how excluded volume interactions affect the configurational averaged velocity field of the fluid. The special case of the frequency-dependent intrinsic viscosity is used to illustrate the type of preaveraging and more general approximations that may be utilized when excluded volume is present. Nevertheless, the calculation of the chain configuration averaged fluid velocity field demonstrates that the generalization from Gaussian chains to polymers with excluded volume merely involves the replacement of the hydrodynamic and force constant matrices by those appropriate to the system with excluded volume. Hence, all previous formal results of the multiple-scattering theory for Gaussian chains can immediately be transcribed to polymers containing excluded volume interactions. (These transcriptions are not all provided herein since they follow directly.) The Gaussian chain theory has already been applied to describe the limiting low-concentration regime, through a concentration expansion, and the higher concentration domain using the effective medium theory. The present paper shows how these previous Gaussian chain formal theoretical solutions are now available for the same concentrations but including excluded volume.

The theory proceeds by introducing a formal solution for the dynamics of a single polymer chain in solution. This dynamical response $\mathbf{g}$ involves an instantaneous contribution to the chain force constants from the excluded volume interactions. The successive scatterings of the fluid flow by chains in solution are expressed by using $\mathbf{g}$. Alternatively, an effective medium method can similarly be introduced to give $\hat{\mathbf{g}}$ describing the chain dynamics in the averaged fluid, where an average has been performed over all other chains in solution.

The dynamical response $\mathbf{g}$ is a nonlinear functional of the stochastic trajectories of the chain segments, and even its Gaussian chain counterpart is generally treated by using a preaveraging approximation. An alternative is provided by numerical simulations, but we consider the appropriate generalization of the preaveraging approximation to systems with excluded volume. Here a number of different approximations emerge because the force constant matrix now depends on the chain dynamics because of excluded volume interactions. The simplest, broken average, approximation is shown to produce a dynamic intrinsic viscosity of the Rouse-Zimm form but in terms of the excluded volume dependent hydrodynamic and force constant matrices. The generalization to higher concentrations automatically follows by use of the effective medium method with screened hydrodynamic interactions and a concentration-dependent equilibrium chain distribution that includes excluded volume screening.

A self-consistent nonuniform scaling approximation to these preaveraged concentration-dependent effective medium equations has been given by Muthukumar and Edwards. However, they have also retained a static approximation, equivalent to replacing the dynamical correlation function (3.38) by its equilibrium $\tau = 0$ limit. Although this approximation grossly simplifies the algebra and preserves qualitative features, it is known to introduce overall errors of factors of 2 in the intrinsic viscosity and infinite dilution relaxation times, so its quantitative applicability at higher concentrations is dubious. The development of a theory free of this static approximation is currently in progress, and some preliminary applications have been given.[8]

The present work provides formally exact solutions for the concentration dependence of dynamical properties of polymers and makes no restrictions concerning the strength of the excluded volume interactions. Hence, it may be utilized along with any systematic procedure for treating excluded volume. One such theory is the chain conformational space renormalization group approach that has been applied to a wide variety of equilibrium and a few nonequilibrium properties of polymers. The theory has been applied in the crossover regime between the Gaussian chain and good solvent limits,[13] and the theory provides all numerical prefactors as well as distribution functions like those for the end-to-end vector[12] and the coherent scattering function.[25] The major limitation of this renormalization group theory is the use of the ϵ-expansion method, which yields poor exponents in a first-order theory. However, a recent second-order crossover calculation for the mean square end-to-end vector has the numerical prefactor close to its first-order value, but the exponents are now very good.[26] There is then hope that a first-order theory with exponents corrected to second order is a quantitatively useful theory.[27] This suggestion deserves further study. Our generalization of the multiple-scattering theory to incorporate excluded volume now provides a wealth of applications of these theories and, of course, tests of their approximations.

The purpose of this paper has been to develop the formal generalization of the multiple-scattering theory containing excluded volume interactions exactly. The above-mentioned calculations of the excluded volume dependent hydrodynamic and force constant matrices are rather formidable in themselves and must be reserved for other works. The former have already been evaluated by renormalization group methods to first order, and we hope to evaluate the latter in the future as well as to combine these together in calculations of the dynamical viscosity, friction coefficient, relaxation spectrum, and their concentration dependence.

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