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Linear Viscoelasticity of Dilute Polymer Solutions in a Viscoelastic Solvent

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ABSTRACT: A theory of linear viscoelasticity is developed for dilute polymer solutions in viscoelastic solvents. The non-Markovian dynamics of a macromolecule with hydrodynamic interaction is analyzed on the basis of a generalized Langevin equation with relaxed friction. The relaxation spectrum (relaxation times and elastic moduli) of the solutions is calculated for a simple viscoelastic model of solvent with a single relaxation time. The theory predicts that at high frequencies the dynamic viscosity of such solutions is less than the zero-shear-rate solvent viscosity.

Introduction

The studies of viscoelastic properties of dilute polymer solutions in low-molecular-weight fluids have a long history.[1−4] Many molecular theories of linear viscoelasticity are usually based on the bead−spring model elaborated by Rouse[5] and Zimm.[6] In this approach, linear chains of elastically connected spherical Brownian particles (beads) model the macromolecules, with the solvent being modeled by a Newtonian fluid. Only a viscous interaction between macromolecule and solvent is involved in this theory, with the Stokes formula employed to describe the hydrodynamic force acting on a spherical particle.

In many cases, it is reasonable to take into account the relaxation effects of solvent.[7−10] An example of a system where these effects are important is a dilute polymer solution in a solvent that is also a polymer.[11,12] Molecular modeling of such solutions allows one to study the effect of viscoelastic reaction of the macromolecule environment on the macroscopic characteristics of the solution. For instance, Volkov and Vinogradov[7] investigated in the free-draining limit the viscoelastic properties of a dilute polymer solution in a simple viscoelastic liquid. However, the hydrodynamic interaction between the segments of a polymer chain cannot also be ignored. In molecular theories of dilute polymer solutions in viscous solvent, this interaction is approximately described by the Oseen tensor.[6,13] Despite the simplicity of such a description, the mathematical difficulties that arise are still enormous. A further simplification is usually made by assuming that, in the limit of linear viscoelasticity, polymer chains are always near equilibrium. The proof of this assumption[13] makes it possible to use in calculations the equilibrium-averaged Oseen tensor.

In the present paper, we apply a generalized Langevin equation with relaxed friction for studying the linear viscoelastic properties of dilute polymer solution in a Maxwell fluid with intramolecular hydrodynamic interaction. The analysis is based on the approach[7] to non-Markovian Brownian motion of Gaussian chain in a simple viscoelastic fluid. This allows us to derive statistical characteristics directly from stochastic equations of macromolecular motion using the fluctuation−dissipation theorem in the position space.

Additionally, we hope that such an approach might help in explaining the high-frequency effects recently found for dilute polymer solutions in low-molecular-weight solvents.[14−16]

Non-Markovian Brownian Dynamics of Macromolecule

In this paper, we use some results of mathematical theory of stochastic processes.[17,18] The simplest and most widely used is the class of stochastic processes of Markovian type where no memory effects are involved in the stochastic description. This means that the increments of process realization for nonoverlapped time intervals should be statistically independent and, therefore, noncorrelated. When it does not happen, a more general but not-so-much elaborated, non-Markovian approach should be employed. This approach is especially important for stochastic modeling of physical processes in very small time intervals where the Markovian assumption of noncorrelatedness is generally invalid. The case of high-frequency macromolecular motions analyzed in this paper is an example of such a stochastic process.

To investigate the statistical properties of long polymer molecules in the flow of a viscoelastic fluid, it is convenient to model a macromolecule by a linear chain of elastically connected Brownian particles. Then, the analysis of this moving polymer chain is reduced to the study of the motion of several points selected on the chain, which are separated by equal (and large enough) contour distances. These points can be considered as spherical Brownian particles (beads). Thus, the real macromolecule is modeled as N subchains of identical length containing certain monomer units, chosen so that the length of each subchain is normally distributed. The macromolecule is then treated as a linear chain of $N + 1$ Brownian particles connected by N harmonic springs. A simple viscoelastic constitutive equation with a single relaxation time, τ_s, models the solvent.

The equation of motion for a macromolecule is expressed as the coupled equations of motion for $N + 1$ beads:

$$\frac{\mathrm{d}r_i^\alpha}{\mathrm{d}t} = u_i^\alpha \qquad m\frac{\mathrm{d}u_i^\alpha}{\mathrm{d}t} = F_i^\alpha + K_i^\alpha + \Phi_i^\alpha \qquad \alpha = [0, N] \quad (1)$$

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Here, the relaxed friction force F^α satisfies the following equation:

$$\tau_s \frac{dF_i^\alpha}{dt} + F_i^\alpha = -\zeta(u_i^\alpha - \mathrm{v}_i^\alpha) \qquad (2)$$

In eqs 1 and 2, m is the mass of bead, $\mathbf{r}^\alpha$ and $\mathbf{u}^\alpha$ are, respectively, the position and velocity of the αth bead, $\mathbf{v}^\alpha$ is the velocity of ambient liquid at the position of αth bead, ζ $(=6\pi a\eta_s)$ is the bead friction coefficient, α is the radius of the bead, and η_s is the solvent viscosity.

The relaxation equation (2) describes the viscoelastic hydrodynamic resistance acting on the spherical Brownian particle in a flow of Maxwell-type viscoelastic fluid. This type of relaxation interaction was first considered for the free-draining case by Volkov and Vinogradov.[7]

The hydrodynamic friction force $\mathbf{F}^\alpha$ arises due to the relative motions of beads and solvent because the solvent velocity v_i^α at αth bead is affected by the motion of the other beads. Owing to the smallness of the bead radius a, one can neglect the terms of the order of $O(a^2)$ related to the fluid inertia contribution in the force $\mathbf{F}^\alpha$. To study the hydrodynamic interaction, we represent the solvent velocity field in eq 2 as

$$v_i^\alpha = v_i^{0\alpha} + v_i'^\alpha \qquad (3)$$

Here, $v_i^{0\alpha} = \nu_{ie} r_e{}^\alpha$ is the unperturbed velocity of the solvent at the location of αth bead, and ν_{ie} is the velocity gradient of solvent flow. The disturbance of solvent velocity, $v_i'^\alpha$, near the αth bead is assumed to be depending linearly on the hydrodynamic forces $\mathbf{F}^\alpha$ acting on all of the beads, other than the αth one. It is calculated for Maxwell fluid using eq A7 from the Appendix as follows:

$$v_i'^\alpha(t) = -T_{ie}^{\alpha\gamma}(\mathbf{r})\left(F_e^\gamma + \tau_s \frac{dF_e^\gamma}{dt}\right) \qquad (4)$$

Here, the Oseen tensor, $T_{ij}^{\alpha\gamma}(\mathbf{r})$, is given by the following:

$$T_{ij}^{\alpha\gamma}(\mathbf{r}) = \frac{1-\delta_{\alpha\gamma}}{8\pi\eta_s \mathbf{r}_{\alpha\gamma}}\left(\delta_{ij} + \frac{r_i^{\alpha\gamma}\, r_j^{\alpha\gamma}}{r_{\alpha\gamma}^2}\right) \qquad r_i^{\alpha\gamma} = r_i^\gamma - r_i^\alpha \qquad (5)$$

In eq 5, $\mathrm{r}_{\alpha\gamma}$ is the length of the vector with the component $r_i^{\alpha\gamma}$ connecting γth and αth beads, and δ_{ij} is the unit tensor. Then, the relaxation equation (2) for hydrodynamic force can be written in the form:

$$\tau_s \frac{dF_i^\alpha}{dt} + F_i^\alpha = -\zeta B_{ie}^{\alpha\gamma}(\mathbf{r})(u_e^\gamma - \nu_{en} r_n^\gamma) \qquad (6)$$

Here,

$$\mathbf{B}(\mathbf{r}) = \mathbf{H}^{-\mathbf{1}}(\mathbf{r}),\ H_{ie}^{\alpha\gamma}(\mathbf{r}) = \delta_{ie}\delta^{\alpha\gamma} + \zeta T_{ie}^{\alpha\gamma}(\mathbf{r})$$

The tensor $\mathbf{T}(\mathbf{r})$, which characterizes hydrodynamic interaction, is a nonlinear function of the bead coordinates. To simplify the problem, we will use the pre-averaging approximation,[6] which replaces $\mathbf{T}(\mathbf{r})$ by its equilibrium-averaged value. Under the Θ-condition, the distribution of $\mathbf{r}^{\alpha\gamma}$ is Gaussian, and the equilibrium-averaged Oseen tensor is represented as

$$\langle T_{ij}^{\alpha\gamma}\rangle_0 = \sqrt{2}h^*(1-\delta_{\alpha\gamma})\delta_{ij}|\alpha-\gamma|^{-1/2} \qquad (7)$$

Then, for the pre-averaged hydrodynamic interaction, the matrix $\mathbf{H}$ has the following simple form:

$$\langle H_{ij}^{\alpha\gamma}(r)\rangle_0 = \mathrm{H}_{\alpha\gamma}\delta_{ij}$$
$$\mathrm{H}_{\alpha\gamma} = \delta_{\alpha\gamma} + \sqrt{2}(1-\delta_{\alpha\gamma})h^*|\alpha-\gamma|^{-1/2} \qquad (8)$$

Here, $\mathrm{H}_{\alpha\gamma}$ is the Zimm hydrodynamic interaction matrix. In eqs 7 and 8, we introduced the nondimensional parameter h^*, which specifies the intensity of hydrodynamic interaction. It is defined as follows:

$$h^* = (\zeta/\eta_s)(12\pi^3 l^2)^{-1/2} \qquad (9)$$

As compared with the Zimm's parameter $h \equiv N^{1/2}h^*$, the use of parameter h^* is advantageous because it is independent of macromolecule size. It is known[19] that for spherical beads $h^* = 0.98a/l$. Thus, h^* is approximately equal to the ratio of the bead radius to the root-mean-square length l of a submolecule. The parameter h^* is expected to range from 0 to about 0.25, which is the nondraining limit.

The elastic (entropy) force acting along the chain on the αth bead is generally defined as $K_i^\alpha(\mathbf{r}) = -\partial \mathrm{U}(\mathbf{r})/\partial r_i^\alpha$. Here $\mathrm{U}(\mathbf{r})$ is the potential of intramolecular interaction. If the subchains are Gaussian and volume effects are excluded, the entropy force is represented as the linear connector:

$$K_i^\alpha = -\ni \mathrm{A}_{\alpha\gamma} r_i^\gamma \qquad \ni = 3T/l^2 \qquad (10)$$

Here, T is the temperature expressed in energy units. The interaction matrix $\mathbf{A}$ is of the following form:

$$\begin{aligned} \mathrm{A}_{\alpha\gamma} &= \delta_{\alpha\gamma} - \delta_{\alpha,\gamma-1} && \alpha = 0 \text{ and } N \\ &= -\delta_{\alpha,\gamma-1} + \delta_{\alpha\gamma} - \delta_{\alpha,\gamma+1} && 0 < \alpha < N \end{aligned} \qquad (11)$$

Because of the thermal motion in the solvent, a Gaussian random force with zero mean value, $\Phi_i^\alpha(t)$, also acts on the chain particles. The statistical properties of $\Phi_i^\alpha(t)$ are completely predetermined by the correlation functions $K_{ik}^{\alpha\gamma}(t) = \langle \Phi_i^\alpha(t)\Phi_k^\gamma(0)\rangle$. The angular brackets denote the averaging over the ensemble of random force realizations. The correlation properties of random forces are intimately associated with the form of the stochastic equations of motion. Because of the fluctuation−dissipation theorem, the Markovian random force $\Phi_i^\alpha(t)$ for a non-Markovian Langevin equation with relaxed friction is found as the solution of the first-order stochastic differential equation:[20]

$$\tau_s \frac{d\Phi_i^\alpha}{dt} + \Phi_i^\alpha = \xi_i^\alpha(t) \qquad (12)$$

Here, the random force $\xi_i^\alpha(t)$ is delta-correlated:

$$\langle \xi_i^\alpha(t)\rangle = 0,\ \langle \xi_i^\alpha(t)\xi_k^\gamma(0)\rangle = 2T\zeta \mathrm{B}^{\alpha\gamma}\delta(t)\delta_{ik} \qquad (13)$$

The initial condition for eq 12 is referred to as $-\infty$, with $\mathrm{B}^{\alpha\gamma}$ being inverse to the Zimm matrix, $\mathrm{H}_{\alpha\gamma}$.

By use of the relaxation eqs 6, 12, and 13 for deterministic (hydrodynamic) and random forces, it is possible to rewrite the initial stochastic eqs 1 and 2 into an equivalent form with a δ-correlated random force:

$$\frac{\mathrm{d}r_i^\alpha}{\mathrm{d}t} = u_i^\alpha \qquad \frac{\mathrm{d}u_i^\alpha}{\mathrm{d}t} = \dot{u}_i^\alpha$$

$$m\tau\frac{\mathrm{d}}{\mathrm{d}t}\dot{u}_i^\alpha + m\dot{u}_i^\alpha = -\zeta B^{\alpha\gamma}(u_i^\gamma - \nu_{ie}r_e^\gamma) + \tau_\mathrm{s}\frac{\mathrm{d}K_i^\alpha}{\mathrm{d}t} + K_i^\alpha + \xi_i^\alpha \quad (14)$$

Because of eq 10, eq 14 takes the following form:

$$m\tau\frac{\mathrm{d}}{\mathrm{d}t}\dot{u}_i^\alpha + m\dot{u}_i^\alpha = -\zeta \mathrm{B}^{\alpha\gamma}(u_i^\gamma - \nu_{ie}r_e^\gamma) - \ni\mathrm{A}_{\alpha\gamma}(r_i^\gamma + \tau_s u_i^\gamma) + \xi_i^\alpha \quad (15)$$

In the equation of motion (15), the set of independent variables includes the first-order acceleration, $\dot{u}_i^\alpha$. This defines a joint Markovian process $\{r_i^\alpha, u_i^\alpha, \dot{u}_i^\alpha\}$. Thus, the problem of Brownian motion of polymer chain with hydrodynamic interaction in a viscoelastic fluid with one relaxation time has been reduced to the statistical description of the dynamical system subjected to a δ-correlated random force. For the sake of mathematical rigor, we have defined all of the above time derivatives of stochastic variables in the sense of generalized functions.

It should be noted that Bird[8] had also attempted to investigate the viscoelastic resistance in the form of eq 2 for dilute polymer solutions in common solvents, with very small relaxation times. However, because of an error in his calculations (see eq 5 in Bird[8]), he missed the important term, similar to $\tau_\mathrm{s}\mathrm{d}K_i^\alpha/\mathrm{d}t$ in our eq 14. As a result, the characteristic relaxation time τ_s of viscoelastic friction did not occur in his final constitutive equation for the solution. In addition, Bird used an incorrect expression for random force that contradicts the fluctuation−dissipation theorem for the non-Markovian Langevin equation (see also Schieber[21]).

Normal Mode Dynamics and Stress Tensor

Statistical characteristics for the non-Markovian stochastic process defined by linearized stochastic eqs 1, 6, 12, and 13 can be determined directly from the above equations. As the first step, we introduce normal coordinates by diagonalizing two symmetric and positively defined matrices **A** and **B** with the orthogonal matrix **Q** as follows: $r_i^\alpha = \mathrm{Q}^{\alpha\gamma}\rho_i^\gamma$. Application of the orthogonal transformation to eqs 1 and 6 yields a set of independent equations:

$$\frac{\mathrm{d}\rho_i^\alpha}{\mathrm{d}t} = \psi_i^\alpha \qquad m\frac{\mathrm{d}\psi_i^\alpha}{\mathrm{d}t} = \Gamma_i^\alpha - \ni\lambda_\alpha\rho_i^\alpha + R_i^\alpha \quad (16)$$

with the relaxed friction for the αth normal mode:

$$\tau_\mathrm{s}\frac{\mathrm{d}\Gamma_i^\alpha}{\mathrm{d}t} + \Gamma_i^\alpha = -\zeta\beta_\alpha(\psi_i^\alpha - \nu_{ie}\rho_e^\alpha) \quad (17)$$

Here, λ_α and β_α are the eigenvalues of the matrices **A** and **B,** respectively, and $\Gamma_i^\alpha = \mathrm{Q}^{\alpha\gamma}F_i^\gamma$ and $R_i^\alpha = \mathrm{Q}^{\alpha\gamma}\Phi_i^\gamma$ are new relaxing and random forces, respectively. The eigenvalues of the interaction matrix **A** are well-known:[4,5]

$$\lambda_\alpha = 4\sin^2\left[\frac{\pi\alpha}{2(N+1)}\right] \qquad (\alpha = 0, 1, 2, ..., N+1) \quad (18)$$

When $\alpha \ll N$, the eigenvalues may approximately be expressed in the form $\lambda_\alpha \approx (\pi\alpha/N)^2$. A normal mode $\rho_i^\alpha(t)$ with $\alpha > 0$ represents the local motion of the chain, which includes $(N + 1)/\alpha$ segments. For large values of α, the eigenvalues β_α in the nondraining limit are of the following form:[3]

$$\beta_\alpha \approx (\alpha/N)^{1/2}/(2h^*) \quad (19)$$

The random forces R_i^α are defined by the Markovian stochastic equations,

$$\tau_\mathrm{s}\frac{\mathrm{d}R_i^\alpha}{\mathrm{d}t} + R_i^\alpha = \varphi_i^\alpha(t) \quad (20)$$

Here, the random forces $\varphi_i^\alpha(t) = \mathrm{Q}_{\gamma\alpha}\xi_i^\gamma(t)$ are δ-correlated:

$$\langle\varphi_i^\alpha(t)\rangle = 0 \qquad \langle\varphi_i^\alpha(t)\varphi_k^\gamma(0)\rangle = 2T\zeta\beta_\alpha\delta_{ik}\delta_{\alpha\gamma} \quad (21)$$

The initial conditions for eq 20 are referred to as $-\infty$. These equations are the result of the fluctuation−dissipation relations (eqs 12 and13) and the transformation properties.

We further assume that the velocity equilibrium is established much faster than the slower process of reaching position equilibrium. The independent stochastic differential equations of motion for beads can then be obtained by projecting the original phase-space stochastic eqs 16 and 17 into position space:

$$2\tau_\alpha\frac{\mathrm{d}\rho_i^\alpha}{\mathrm{d}t} - 2\tau_\alpha^\mathrm{Z}\nu_{ie}\rho_e^\alpha + \rho_i^\alpha = \frac{h_i^\alpha}{\ni\lambda_\alpha} \quad (22)$$

Here, the relaxation times τ_α are defined as follows:

$$\tau_\alpha = \tau_s/2 + \tau_\alpha^\mathrm{Z} \qquad \tau_\alpha^\mathrm{Z} = \zeta\beta_\alpha/2\ni\lambda_\alpha \quad (23)$$

where τ_α^Z are the known Zimm relaxation times. In the case of free-draining polymer chains, $\beta_\alpha = 1$, and the Zimm relaxation times τ_α^Z are reduced to the Rouse relaxation times.

Unlike the Markovian stochastic equations, in our non-Markovian case, the statistical properties of random forces $h_i^\alpha(t)$ in position space (for noninertial approximation) are different from those established above for the complete inertial case. To determine them, we note that the correlation functions $K_{ik}^h(t) = \langle h_i^\alpha(t)h_k^\gamma(0)\rangle$ of random forces $h_i^\alpha(t)$ are defined by the dynamics established for the quiescent system:

$$2\tau_\alpha\frac{\mathrm{d}\rho_i^\alpha}{\mathrm{d}t} + \rho_i^\alpha = \frac{h_i^\alpha}{\ni\lambda_\alpha} \quad (24)$$

Applying the Fourier transform for the random functions $\rho_i^\alpha(t)$ and $h_i^\alpha(t)$ yields the Langevin equation for the spectral amplitudes:

$$\chi_\alpha^{-1}[\omega]\rho_i^\alpha(\omega) = h_i^\alpha(\omega) \quad (25)$$

Here, the following notations for the two- and one-sided Fourier transforms are used:

$$x(\omega) = \int_{-\infty}^{\infty} x(t)e^{i\omega t}\mathrm{d}t \qquad x[\omega] = \int_0^{\infty} x(t)e^{i\omega t}\,\mathrm{d}t$$

The susceptibility of the system has the following form:

$$\chi_\alpha[\omega] = \frac{1}{\ni\lambda_\alpha}\frac{1}{1 - i\omega 2\tau_\alpha} \tag{26}$$

The statistical properties of the random forces $h_i^\alpha(t)$ can be determined with the help of the Callen–Welton fluctuation–dissipation theorem. The common formulation of the theorem given by Landau and Lifshitz[22] is

$$K_{ik}^h(\omega) = \frac{iT}{\omega}(\chi_\alpha^{-1}[\omega] - \chi_\alpha^{-1}[-\omega])\delta_{ik} \tag{27}$$

Substituting the specific expression for susceptibility (eq 26), we find from eq 27 that the correlation function of the random force $h_i^\alpha(t)$ is

$$\langle h_i^\alpha(t) h_k^\alpha(0)\rangle = 4/T\ni\lambda_\alpha\tau_\alpha\delta(t)\delta_{ik}\delta_{\alpha\gamma} \tag{28}$$

By using eqs 22 and 28, it is easy to derive the equation for the evolution of a one-time moment of normal coordinates $\langle\rho_i^\alpha(t)\rho_k^\alpha(t)\rangle$, which defines the stress tensor in the system:

$$\tau_\alpha\frac{\mathrm{d}}{\mathrm{d}t}\langle\rho_i^\alpha(t)\rho_k^\alpha(t)\rangle + \langle\rho_i^\alpha(t)\rho_k^\alpha(t)\rangle - \frac{1}{2\ni\lambda_\alpha}(\langle h_i^\alpha(t)\rho_k^\alpha(t)\rangle + \langle h_k^\alpha(t)\rho_i^\alpha(t)\rangle) = \frac{2}{3}\tau_\alpha^Z\langle\rho^\alpha\rho^\alpha\rangle_0\gamma_{ik} \tag{29}$$

Here, $\gamma_{ik} = (\nu_{ik} + \nu_{ki})/2$ is the strain rate tensor. The right-hand side in eq 29 describes the equilibrium value of the one-time moments as follows:

$$\langle\rho_i^\alpha(t)\rho_k^\alpha(t)\rangle_0 = \langle\rho^\alpha\rho^\alpha\rangle_0\delta_{ik}/3$$

The unknown value $\langle h_i^\alpha(t)\rho_k^\alpha(t)\rangle$ in eq 29 is calculated with the use of the Furutsu–Novikov formula,[23] which in our case has the following form:

$$\langle h_i^\alpha(t)\rho_k^\alpha(t)\rangle = \int_0^t\langle h_i^\alpha(t)h_e^\gamma(s)\rangle\frac{\delta\rho_k^\alpha(t)}{\delta h_e^\gamma(s)}\mathrm{d}s \tag{30}$$

Calculating the functional derivative with the use of eq 24,

$$\frac{\delta\rho_k^\alpha(t)}{\delta h_e^\gamma(t)} = \frac{1}{2\ni\lambda_\alpha\tau_\alpha}\delta_{ke}\delta_{\alpha\gamma} \tag{31}$$

and employing the fluctuation–dissipation relation (eq 28), results in the following: $\langle h_i^\alpha(t)\rho_k^\alpha(t)\rangle = T\delta_{ik}$. As a result of these calculations, the closed form of the kinetic equation for the one-time moments is obtained as follows:

$$\tau_\alpha\frac{\mathrm{d}}{\mathrm{d}t}\langle\rho_i^\alpha(t)\rho_k^\alpha(t)\rangle + \langle\rho_i^\alpha(t)\rho_k^\alpha(t)\rangle - \frac{T}{\ni\lambda_\alpha}\delta_{ik} = \frac{2}{3}\tau_\alpha^Z\langle\rho^\alpha\rho^\alpha\rangle_0\gamma_{ik} \tag{32}$$

The equilibrium values of normal coordinate moments found from this equation are the following:

$$\langle\rho_i^\alpha\rho_k^\alpha\rangle_0 = \frac{T}{\ni\lambda_\alpha}\delta_{ik} \tag{33}$$

These moments describe the shape and size of the macromolecule unperturbed by the flow of the solvent. Their values are the same in both the viscous and viscoelastic solvents. Because eq 33 yields $\langle\rho^\alpha\rho^\alpha\rangle_0 = 3T/(\ni\lambda_\alpha)$, the final form of relaxation eq 32 is represented as follows:

$$\tau_\alpha\frac{\mathrm{d}}{\mathrm{d}t}\langle\rho_i^\alpha(t)\rho_k^\alpha(t)\rangle + \langle\rho_i^\alpha(t)\rho_k^\alpha(t)\rangle - \frac{T}{\ni\lambda_\alpha}\delta_{ik} = \frac{2T}{\ni\lambda_\alpha}\tau_\alpha^Z\gamma_{ik} \tag{34}$$

The solution of this equation with the equilibrium initial condition is the following:

$$\langle\rho_i^\alpha(t)\rho_k^\alpha(t)\rangle = \frac{T}{\ni\lambda_\alpha}\delta_{ik} + \frac{2T}{\ni\lambda_\alpha}\int_0^\infty\eta_\alpha(s)\gamma_{ik}(t-s)\,\mathrm{d}s \tag{35}$$

Here the relaxation function, $\eta_\alpha(t)$, has the following form:

$$\eta_\alpha(t) = (\tau_\alpha^Z/\tau_\alpha)\exp(-t/\tau_\alpha) \tag{36}$$

We now obtain the complete set of equations that macroscopically describe flows of dilute polymer solutions. These equations can be derived using the two-fluid model for the polymer–solvent system.[7,24,25] By following this model, the stress tensor for solution is represented as the sum of solvent and polymer contributions (marked by upper indexes s and p, respectively):

$$\sigma_{ij} = \sigma_{ij}^s + \sigma_{ij}^p \tag{37}$$

The stress tensor σ_{ij}^s is determined by direct averaging of the stress tensor of the carrying solvent:

$$\sigma_{ij}^s = -p^s\delta_{ij} + 2\int_0^\infty G^s(t')\gamma_{ij}^s(t-t')\,\mathrm{d}t' \tag{38}$$

Here p^s is the partial pressure and $\gamma_{ij}^s = \mathrm{v}_{(i,j)}^s$. For the Maxwell solvent, the relaxation function is the following:

$$G^s(t) = (\eta_s/\tau_s)\exp(-t/\tau_s) \tag{39}$$

The expression for the polymer contribution in the stress tensor, σ_{ij}^p, is the following:

$$\sigma_{ij}^p = -nT\delta_{ij} + n\sum_{\alpha=1}^N\ni\lambda_\alpha(\langle\rho_i^\alpha\,\rho_j^\alpha\rangle - \langle\rho_i^\alpha\,\rho_j^\alpha\rangle_0) \tag{40}$$

Here n is the amount of macromolecules in unit volume. Equation 40 has been calculated by Volkov and Vinogradov[7] directly from the stochastic equation of motion for a single macromolecule, without recourse to the corresponding equation for the distribution function usually employed in the traditional Kirkwood method.

Equations 35, 36, 38, and 40 define the total stress tensor for a dilute polymer solution in a Maxwell solvent:

$$\sigma_{ij} = -p\delta_{ij} + 2\int_0^\infty G(s)\gamma_{ij}(t-s)\,\mathrm{d}s$$

$$G(t) = G^s(t) + G^p(t) \tag{41}$$

Here $G(t)$ is the relaxation modulus for the solution. The polymer contribution to the relaxation modulus is defined by the following:

$$G^p(t) = \sum_{\alpha=1}^N G_\alpha\exp(-t/\tau_\alpha) \qquad G_\alpha = nT\tau_\alpha^Z/\tau_\alpha \tag{42}$$

It is remarkable that the partial moduli G_α depend on parameter α.

Dynamic Viscoelastic Properties

The complex shear modulus of dilute polymer solution in a Maxwell fluid is found due to eqs 39 and 42 as

$$G[\omega] = G^{s}[\omega] + nT\sum_{\alpha=1}^{N}\frac{\tau_\alpha^{Z}}{\tau_\alpha}\frac{-i\omega\tau_\alpha}{1 - i\omega\tau_\alpha}$$
$$G^{s}[\omega] = \frac{-i\omega\eta_s}{1 - i\omega\tau_s} \qquad (43)$$

Using eq 43, we now introduce the dimensionless intrinsic storage and loss moduli for the dilute polymer solution in the viscoelastic solvent:

$$[G']_R \equiv \frac{G'[\omega] - G'_s[\omega]}{nT} = \sum_{\alpha=1}^{N}\frac{\tau_\alpha^{Z}}{\tau_\alpha}\frac{(\omega\tau_\alpha)^2}{1 + (\omega\tau_\alpha)^2}$$
$$[G'']_R \equiv \frac{G''[\omega] - G'_s[\omega]}{nT} = \sum_{\alpha=1}^{N}\frac{\tau_\alpha^{Z}}{\tau_\alpha}\frac{\omega\tau_\alpha}{1 + (\omega\tau_\alpha)^2} \qquad (44)$$

In the free-draining case, eq 44 takes the following form:

$$[G']_R = \sum_{\alpha=1}^{N}\frac{1}{1 + \chi_R\alpha^2}\frac{(\omega_R\theta_\alpha^R)^2}{1 + (\omega_R\theta_\alpha^R)^2}$$
$$[G'']_R = \sum_{\alpha=1}^{N}\frac{1}{1 + \chi_R\alpha^2}\frac{\omega_R\theta_\alpha^R}{1 + (\omega_R\theta_\alpha^R)^2} \qquad (45)$$
$$\omega_R = \omega\tau_1^R \qquad \tau_1^R = \zeta(lN)^2/(6\pi^2 T)$$

Here, ω_R is a dimensionless frequency, and τ_1^R is the terminal (or longest) Rouse relaxation time. The dimensionless relaxation times, θ_α^R, of the dilute polymer solution in the Maxwell solvent and the dimensionless parameter χ_R are defined as

$$\theta_\alpha^R \equiv \tau_\alpha/\tau_1^R = (1 + \chi_R\alpha^2)/\alpha^2 \qquad \chi_R = \tau_s/2\tau_1^R \qquad (46)$$

Calculation of the intrinsic moduli of a dilute polymer solution with hydrodynamic interaction is more complicated. In eq 46, the analytical expressions for the relaxation times can only be written for $N = 2$ and 3. Because of eq 23, the dimensionless relaxation times θ_α^Z are

$$\theta_\alpha^Z = \chi_Z + \bar{\tau}_\alpha^Z \qquad (\chi_Z = \tau_s/2\tau_1^Z;\ \bar{\tau}_\alpha^Z = \tau_\alpha^Z/\tau_1^Z) \qquad (47)$$

The reduced Zimm relaxation times $\bar{\tau}_\alpha^Z$ are expressed in terms of the eigenvalues λ_α of the matrix **A·H** as

$$\bar{\tau}_\alpha^Z = \lambda_1/\lambda_\alpha \qquad \tau_1^Z = \zeta/2\ni\lambda_1 \qquad (48)$$

Here, τ_1^Z is the Zimm terminal relaxation time. In the case of dominant hydrodynamic interaction when $h^* \gg 1$, the expression for λ_α is[6]

$$\lambda_\alpha = 4h\lambda'_\alpha/N^2 \qquad (49)$$

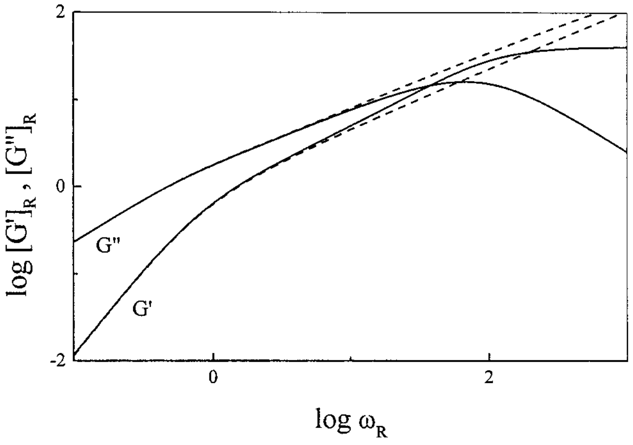

Figure 1. Reduced intrinsic moduli plotted logarithmically against reduced frequency for dilute polymer solutions in viscous (dashed lines) and viscoelastic (solid lines) solvents.

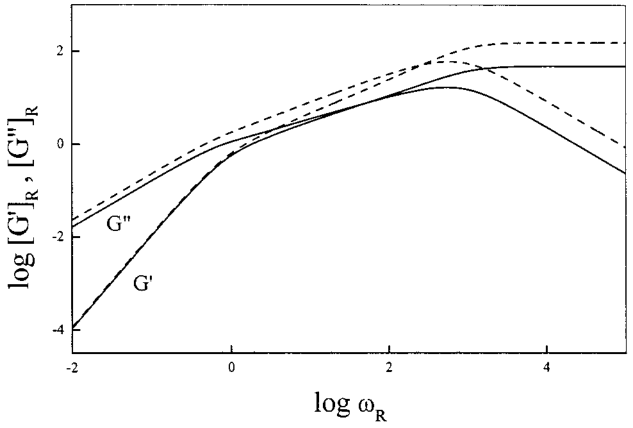

Figure 2. Polymer contribution in the storage and loss moduli for a dilute polymer solution as a function of the dimensionless frequency ω_R for free-draining coils with $\chi_R = 10^{-3}$ (solid lines) and dominant hydrodynamic interaction with $\chi_Z = 10^{-3}$ (dashed lines).

The first six λ'_α's have been tabulated.[26] When $\alpha > 6$, λ'_α's are represented by the following asymptotic formula:

$$\lambda'_\alpha = \pi^2\alpha^{3/2}/2 \qquad (50)$$

Figure 1 demonstrates the plots of reduced intrinsic moduli $[G']_R$ and $[G'']_R$ versus the dimensionless frequency, $\omega_R = \omega\tau_1^Z$. The plots have been calculated taking into account hydrodynamic interaction in the presence and the absence of solvent viscoelasticity. The dashed and solid lines represent, respectively, the predictions of the Zimm theory and the present theory with $\chi_Z = 10^{-2}$. Figure 1 shows that the elasticity of solvent is important only at high frequencies. This result is physically evident because, with increasing frequency, the viscoelastic reaction of solvent to the motion of macromolecules changes from almost viscous to almost elastic.

Figures 2 and 3 show the plots of the intrinsic storage $[G']_R$ and loss moduli $[G'']_R$ versus the dimensionless frequency ω_R in the free-draining ($\omega_R = \omega\tau_1^R$) and the hydrodynamic interaction ($\omega_R = \omega\tau_1^Z$) cases. The dependencies of the intrinsic moduli on frequency are specified by the parameters χ_R and χ_Z. These are the ratios of the characteristic relaxation times of viscoelastic solvent and macromolecule in viscous solvent. There

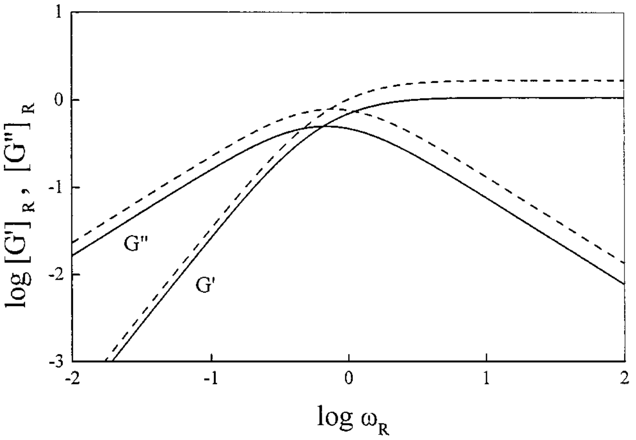

Figure 3. Logarithmic plots of dimensionless intrinsic storage and loss moduli vs nondimensional frequency ω_R for values of the parameters: $\chi_R = 1$ (solid) and $\chi_Z = 1$ (dashed lines).

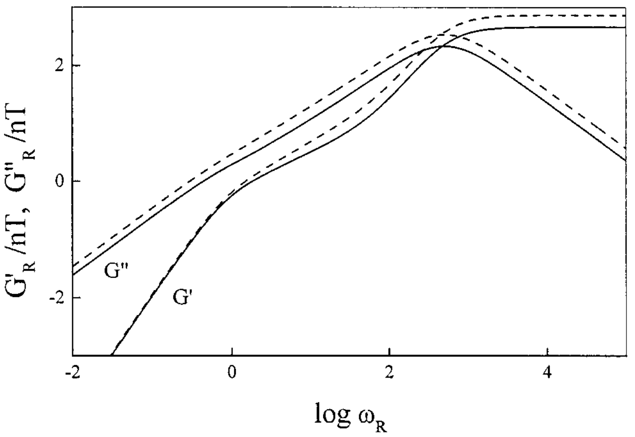

Figure 4. Logarithmic plots of dimensionless total storage and loss moduli vs reduced frequency for free-draining coils with $\chi_R = 10^{-3}$ (solid lines) and dominant hydrodynamic interaction with $\chi_Z = 10^{-3}$ (dashed lines).

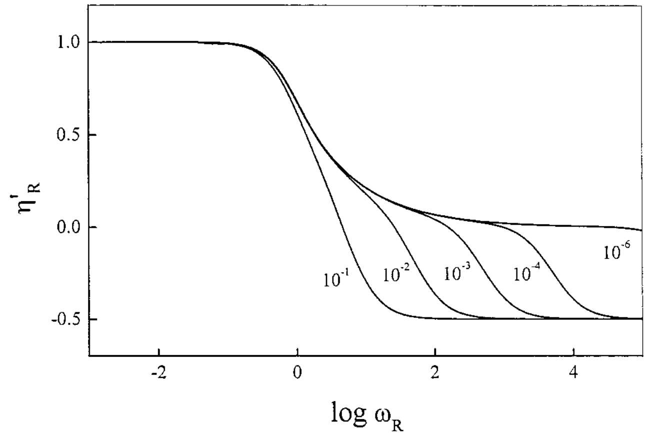

Figure 5. Plots of normalized dynamic viscosity η'_R vs log ω_R for values χ_R indicated with figures at the curves and $\eta_s/\eta_0 = {}^1/_3$.

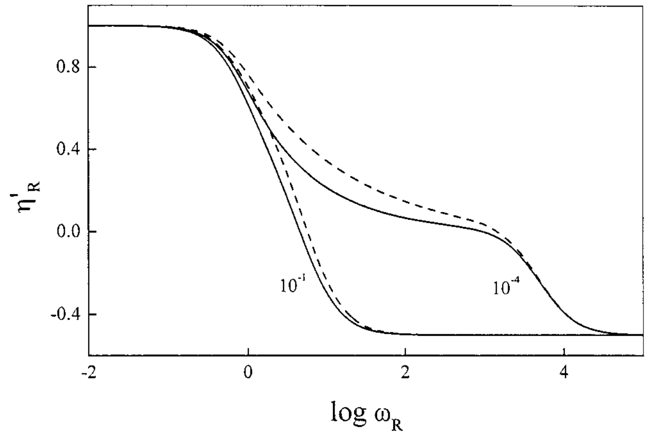

Figure 6. Plots of normalized dynamic viscosity η'_R vs log ω_R for the free-draining (solid lines) and nondraining (dashed lines) polymer chains when $\chi_R = \chi_Z = 10^{-1}$ and 10^{-4} and $\eta_s/\eta_0 = {}^1/_3$.

are two types of dilute polymer solutions in the viscoelastic solvent. The first type describes the solvent with a small characteristic relaxation time when χ_R and $\chi_Z < 1$. Figure 2 shows the results of the calculation for the value of $\chi_R = \chi_Z = 10^{-3}$. One can see progressive deviations from the Rouse square-root proportionality to ω (for the free-draining case) and from the Zimm law $\omega^{2/3}$ (for the nondraining polymer chains) when frequency increases. In both cases, $[G']_R$ approaches a limit value $[G']_p$, with $[G'']_R$ passing through a maximum, $[G'']_m$, at high frequencies. Note that for large values of the number N of beads in the model, the values of $[G']_p$ and $[G'']_m$ are independent of N.

Figure 3 shows the reduced intrinsic moduli for the solutions with a slow relaxed solvent when $\chi_R = \chi_Z = 1$. In this case, the frequency dependencies display a distinct deviation from the Rouse and Zimm theories. Similar behavior was also found for $[G']_R$ and $[G'']_R$ when χ_R and $\chi_Z > 1$. The intrinsic moduli for such dilute solutions have the same features as the linear viscoelastic characteristics of monodisperse high-molecular-weight linear polymers in slow relaxation region.

The shapes of the resulting curves $G'_R = G'/nT$ and $G''_R = G''/nT$ for $\chi_R = \chi_Z = 10^{-3}$ and $\eta_s/\eta_0 = {}^1/_3$ are shown in Figure 4. Here, η_0 is the zero-shear-rate viscosity of solution. The solid and dashed curves represent the predictions of the theory for the free-draining and nondraining polymer chains, respectively. The calculated dashed curves are based on the original Zimm eigenvalues.

The expression for the normalized dynamic viscosity $\eta'(=G''/\omega)$ of dilute polymer solution in Maxwell solvent is

$$\eta'_R = \frac{\eta' - \eta_s}{\eta_0 - \eta_s} = -\frac{\eta_s}{\eta_0 - \eta_s}\frac{(\omega\tau_s)^2}{1 + (\omega\tau_s)^2} + \sum_{\alpha=1}^{N}\frac{\tau^Z_\alpha/\sum_{r=1}^{N}\tau^Z_r}{1 + (\omega\tau_\alpha)^2}$$

$$\eta_0 = \eta_s + nT\sum_{\alpha=1}^{N}\tau^Z_\alpha \quad (51)$$

Here, η_0 is the zero-shear-rate viscosity of solution.

The dimensionless frequency dependence of η'_R for various values of χ_R and $\eta_s/\eta_0 = {}^1/_3$ is illustrated in Figure 5 for the free-draining case. The most important observation from this calculation is that η'_R approaches the negative limit, $-\eta_s/(\eta_0 - \eta_s)$ at high values of ω. This effect is larger for solvents with long relaxation times.

The effect of hydrodynamic interaction on the dynamic viscosity is shown in Figure 6. It is seen that the effect decreases when the solvent relaxation time increases.

Conclusion and Discussion

The hydrodynamic interaction between segments of macromolecule moving in a linear viscoelastic fluid has been considered. A modified Oseen expression has been derived for the flow of viscoelastic fluid due to the action of a time-dependent force highly localized in space. The effect of the hydrodynamic interaction on the linear viscoelastic behavior of dilute polymer solution in a viscoelastic solvent with a single relaxation time has then been analyzed. Statistical properties of motion of a Gaussian chain in the Maxwell fluid were studied using a non-Markovian Langevin equation with relaxed friction. This approach resulted in calculations of dynamic moduli for the solution. Two different types of viscoelastic behavior for dilute polymer solutions in Maxwell solvent were found depending on the value of the solvent's relaxation time, τ_s. When the value of τ_s is relatively small, the dilute solutions of polymers in viscoelastic solvent display rheological behavior similar to that for dilute polymer solutions in low-molecular-weight fluids. When the value of τ_s is relatively large, the viscoelastic properties of dilute polymer solutions are reminiscent of those for monodisperse linear polymers of high molecular weight in the slow relaxation region.

Our calculations showed that the high-frequency dynamic viscosity of dilute polymer solution in Maxwell solvent is less than the zero-shear-rate solvent viscosity (however, it is not less than the solvent dynamic viscosity).

It has been observed that at high frequencies the dynamic viscosity of dilute polymer solutions in some low-molecular-weight solvents was less than the solvent's viscosity.[14-16] Some authors[14-16] have denied the solvent viscoelastic properties as the possible reason for the effect, because the pure solvent displayed no visible viscoelasticity in their experimental frequency range. Therefore, they assumed that the presence of macromolecules in solution might modify the solvent's dynamics near a single chain. If this is the case, the application of the present model for theoretical explanation of the effects[14-16] cannot be used directly nor considered other than an effective phenomenological description. However, we cannot rule out another possibility related to the existence of a low-molecular-weight polymer fraction always present in the bulk solution after the polymer has dissolved. If this is the case, the viscoelastic properties of the solvent in solution can dramatically be changed in comparison with those of the pure solvent. In this case, a high-frequency, almost elastic response of a solvent on the motion of macromolecules, which has mostly been considered in the present paper, can explain this effect. Additionally, at least a partial explanation of the effect might be caused by the small-scale intramolecular motions that in terms of Brownian dynamics can be modeled by an inner viscoelasticity (e.g., see Bixon[27] and Volkov et al.[28]).

Appendix: Hydrodynamic Interaction in a Viscoelastic Fluid

Consider the effect of hydrodynamic interaction for an incompressible viscoelastic fluid with the following general linear constitutive equation:

$$\sigma_{ij} = -p\delta_{ij} + 2\int_0^\infty \eta(s)\gamma_{ij}(t-s)\,\mathrm{d}s \qquad \text{(A1)}$$

Here, $\eta(s)$ is the relaxation function, and p is the pressure. Our purpose is to calculate the time-dependent velocity field $\mathbf{v}(\mathbf{x},t)$, created by an external time-dependent body force $\mathbf{F}(\mathbf{x},t)$. We assume that the inertia effects are negligibly small; i.e., the Stokes equations are valid:

$$\frac{\partial\sigma_{ij}}{\partial x_j} + F_i(\mathbf{x},t) = 0 \qquad \nu_{i,i} = 0 \qquad \text{(A2)}$$

These equations are easily solved with the use of the space-time Fourier transform

$$g(\mathbf{k},\omega) = \int_{-\infty}^{\infty} \mathrm{d}t \int \mathrm{d}\mathbf{x}\, g(\mathbf{x},t)e^{i(\mathbf{k}\cdot\mathbf{x}+\omega t)}$$

to obtain

$$\mathbf{v}(\mathbf{x},\omega) = \int \mathrm{d}\mathbf{x}'\mathbf{T}(\mathbf{x}-\mathbf{x}',\omega)\cdot\mathbf{F}(\mathbf{x}',\omega)$$
$$\mathbf{T}(\mathbf{x},\omega) = \mathbf{H}(\mathbf{x})/\eta[\omega] \qquad \text{(A3)}$$

Here, $\eta[\omega]$ is the complex viscosity of fluid defined by the one-sided Fourier transform of the relaxation function $\eta[s]$, and the hydrodynamic interaction tensor $\mathbf{H}$ in eq A3 is given by[3]

$$\mathbf{H}(\mathbf{x}) = \frac{1}{8\pi x}\left(\mathbf{I} + \frac{\mathbf{xx}}{x^2}\right) \qquad x = |\mathbf{x}| \qquad \text{(A4)}$$

We now consider the special case of a time-dependent *point force*, which acts at a stationary position $\mathbf{r}$: $\mathbf{F}(\mathbf{x} - \mathbf{r},t) = \mathbf{F}(t)\delta(\mathbf{x} - \mathbf{r})$. Equation A3 is then reduced to the following simple form:

$$\mathbf{v}(\mathbf{x},\omega) = \mathbf{T}(\mathbf{x}-\mathbf{r},\omega)\cdot\mathbf{F}(\omega) \qquad \text{(A5)}$$

Consider now the particular case of Maxwell fluid where

$$\eta[\omega] = \eta/(1 - i\omega\tau) \qquad \text{(A6)}$$

Here, η is the viscosity, and τ is the relaxation time. Because of eqs A5 and A6, the fluid velocity at a point $\mathbf{x}$ when force acts on the fluid at the point $\mathbf{r}$ is

$$\mathbf{v}(\mathbf{x},t) = \mathbf{H}(\mathbf{x}-\mathbf{r})\cdot\left(\mathbf{F} + \tau\frac{\mathrm{d}\mathbf{F}}{\mathrm{d}t}\right)/\eta \qquad \text{(A7)}$$

For a viscoelastic fluid with a spectrum of relaxation times, eq A5 yields the integral relation:

$$\mathbf{v}(\mathbf{x},t) = \mathbf{H}(\mathbf{x}-\mathbf{r})\cdot\int_0^\infty J(s)\mathbf{F}(t-s)\,\mathrm{d}s \qquad \text{(A8)}$$

Here, $J(s)$ is the function defined by the one-sided Fourier transform $J[\omega] = 1/\eta[\omega]$.

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