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# EQUATIONS OF MOTION OF CONCENTRATED POLYMER SOLUTIONS

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We establish a very simple system of controlling equations to describe the motion of viscoelastic media.

1. The problem of the equations of motion of concentrated polymer solutions to describe the motion of systems exhibiting viscoelastic properties has not been completely solved; there are differences of opinion with regard to the form of the nonlinear controlling equation [1]. Since there is no general form of the rheological relation for all viscoelastic systems, research is necessary based on structural concepts and relating the nonlinear behavior of concentrated solutions to the characteristics of the behavior of macromolecules in the system (deformability, kinetic, rigidity, etc.) taken into account in one form or another. A simple approach to the description of the motion of concentrated solutions based on an analysis of the behavior of dumbbells in a viscous medium is the simplest model of a structural element of the system [2]. When internal viscosity is taken into account, the controlling relations include the stress tensor $\sigma_{ik}$ expressed in terms of the moments of the distribution function, and a system of equations for the moments [2], which is generally not closed:

$$\sigma_{ik} = -p\delta_{ik} + 2\eta_E\gamma_{ik} + \frac{1}{2}n\zeta\left[\frac{1}{\tau'}\left(\langle \rho_i\rho_k) - \frac{3}{4\mu}\langle e_s e_k\rangle\right) + \frac{1}{\tau_D}\frac{3}{4\mu}\left(\langle e_i e_k\rangle - \frac{1}{3}\delta_{ik}\right) + \frac{2\lambda}{\lambda+\zeta}\langle \rho_i\rho_k e_j e_s\rangle\gamma_{js}\right], \tag{1}$$

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$$\frac{d\langle \rho_i\rho_k\rangle}{dt} = -\frac{1}{\tau_D}\frac{3}{4\mu}\left(\langle e_ie_k\rangle - \frac{1}{3}\delta_{ik}\right) - \frac{1}{\tau'}\left(\langle \rho_i\rho_k\rangle - \right.$$

$$\left. -\frac{3}{4\mu}\langle e_ie_k\rangle\right) + \nu_{ij}\langle \rho_k\rho_j\rangle + \nu_{kj}\langle \rho_j\rho_i\rangle - \frac{2\lambda}{\lambda+\zeta}\langle \rho_i\rho_ke_je_s\rangle\gamma_{js}, \tag{2}$$

$$\frac{d\langle e_ie_k\rangle}{dt} = -\frac{1}{\tau_D}\left(\langle e_ie_k\rangle - \frac{1}{3}\delta_{ik}\right) + \nu_{is}\langle e_se_k\rangle + \nu_{ks}\langle e_se_i\rangle - 2\langle e_ie_ke_je_s\rangle\gamma_{js}. \tag{3}$$

We present the equations for the moments of lowest order. Angle brackets denote the average over orientations.

The system given above describes the basic nonlinear effects in the flow of polymers [2, 3], and therefore can be used to study polymers under complex deformation conditions. However, it remains unclear which element of the moving medium corresponds to the dumbbells. Equations (1)-(3) contain parameters which are essentially phenomenological constants whose significance and molecular meaning must be refined.

In the present article we determine the parameters of the system of equations on the basis of a detailed model of the behavior of a macromolecule in the system [4], and write the equations of motion of concentrated polymer solutions in concrete form.

2. The equation of the dynamics of a macromolecule which is modeled by a chain of N + 1 Brownian particles moving in a viscoelastic medium, written in normal coordinates in which the binding of the particles in the chain is not taken into account, has the form

$$m\frac{d^2\rho_i^\nu}{dt^2} = -\int_0^\infty \beta_\nu(s)(\dot{\rho}_i^\nu - \nu_{ij}\rho_j^\nu)_{t-s}ds - \int_0^\infty \varphi_\nu(s)(\dot{\rho}_i^\nu - \omega_{ij}\rho_j^\nu)_{t-s}ds - 2T\mu'\alpha_\nu\rho_i^\nu + R_{\gamma\nu}\Phi_i^\gamma. \tag{4}$$

Equation (4) satisfactorily describes [4] the observed distribution of relaxation times and the dependence of the linear viscoelasticity of linear polymers on the molecular mass. To do this it turned out to be sufficient to assume that microviscoelasticity is characterized by a single relaxation time $\tau$, i.e.

$$\beta_\nu(s) = \zeta\left[2\delta(s) + \frac{B}{\tau}\exp(-s/\tau)\right], \quad \varphi_\nu(s) = \zeta\frac{E}{\tau}\exp(-s/\tau).$$

We note that in the case under consideration the "internal" viscosity of a macromolecule is not related to conformational transitions, but to the deformation of the surrounding macromolecules, and therefore "internal" and "external" viscoelasticity are characterized by a single relaxation time.

The dynamics of a macromolecule is described in less detail by the average values of the moments, for example, the second-order moment, which is given by (4), and has the form

$$\langle \rho_i^\nu\rho_k^\nu\rangle = \frac{1}{2\mu'\alpha_\nu} + 2\int_0^\infty [R\exp(-s/\tau_\nu^+) + F\exp(-s/\tau_\nu^0) + G\exp(-s/\tau_\nu^-)]\gamma_{ik}(t-s)\,ds,$$

where we have introduced the notation

$$\tau_\nu^+ = \tau^*k(1+\sqrt{1-p}),\ \tau_\nu^- = \tau^*k(1-\sqrt{1-p}),\ \tau_\nu^0 = \frac{2\tau_\nu^+\tau_\nu^-}{\tau_\nu^+ + \tau_\nu^-},$$

$$R = \frac{1}{\alpha_\nu}\left(\frac{v}{\chi}\right)^2\left[1 - \frac{\chi}{k(1+\sqrt{1-p})} + B^{-1}\right]\left[1 + \psi - \frac{\chi}{k(1+\sqrt{1-p})} + B^{-1}\right],$$

$$G = \frac{1}{\alpha_\nu}\left(\frac{v}{\chi}\right)^2\left[1 - \frac{\chi}{k(1-\sqrt{1-p})} + B^{-1}\right]\left[1 + \psi - \frac{\chi}{k(1-\sqrt{1-p})} + B^{-1}\right],$$

$$F = -\frac{1}{\alpha_\nu}\left(\frac{v}{\chi}\right)^2\left\{\left[1 - \frac{\chi}{k(1+\sqrt{1-p})} + B^{-1}\right]\left[1 + \psi - \frac{\chi}{k(1-\sqrt{1-p})} + B^{-1}\right] + \right.$$

$$\left. + \left[1 - \frac{\chi}{k(1-\sqrt{1-p})} + B^{-1}\right]\left[1 + \psi - \frac{\chi}{k(1+\sqrt{1-p})} + B^{-1}\right]\right\},$$

$$k = \frac{B}{2\nu^2}(1 + \psi + \nu^2\chi + B^{-1}),\quad p = \frac{4\nu^2\chi}{B(1 + \psi + \nu^2\chi + B^{-1})^2},\quad \chi = \frac{\tau}{2B\tau^*},$$

$$\psi = \frac{E}{B}, \quad v = \frac{kp}{2\sqrt{1-p}}, \quad \tau^* = \frac{\zeta N^2}{4T\mu'\pi^2},$$

$$\mu' = \frac{3N}{2\langle L^2 \rangle}, \quad \alpha_\nu = \left(\frac{\pi\nu}{N}\right)^2.$$

Thus, a macromolecule is characterized by a set of relaxation times

$$\tau_\nu^+ = \tau^* k(1+\sqrt{1-p}), \quad \tau_\nu^- = \tau^* k(1-\sqrt{1-p}), \quad \tau_\nu^0 = \tau^* kp,$$

which for $p \ll 1$ takes the form

$$\tau_\nu^+ = 2\tau^* k(1 - p/4), \quad \tau_\nu^- = \frac{1}{2}\tau^* kp, \quad \tau_\nu^0 = \tau^* kp.$$

A characteristic feature of the relaxation spectrum obtained is its resolution into a group of short and a group of long times close to one another.

3. In order to compare the results presented with the results for dumbbells, it is necessary to introduce the approximation of a single relaxation time, which can be defined as the longest relaxation time of the inertia tensor of a macromolecule:

$$\langle S_i S_k \rangle = \frac{1}{N+1} \sum_{\nu=1}^{N} \langle \rho_i^\nu \rho_k^\nu \rangle .$$

We compare this value with the dumbbell moment $\langle \rho_i \rho_k \rangle$ given by Eq. (2). In the linear approximation we find (more details in [2]):

$$\langle \rho_i \rho_k \rangle = \frac{\delta_{ik}}{4\mu} + \frac{5\zeta + 3\lambda}{10\mu(\lambda+\zeta)} \int_0^\infty \exp(-y/\tau_D)\, \gamma_{ik}(t-y)\, dy -$$

$$- \frac{12}{5} \frac{T\lambda}{\zeta(\lambda+\zeta)} \int_0^\infty \exp(-y/\tau') \int_0^\infty \exp(-z/\tau_D)\, \gamma_{ik}(t-y-z)\, dz dy.$$

In order to obtain an expression for the relaxation time, we compare the change in quantities relative to their equilibrium values. For oscillating shear flow in which $\gamma_{ik}(t) \sim \exp(-i\omega t)$, the ratios under consideration can be written in the form

$$3\langle S_i S_k \rangle / \langle S^2 \rangle_0 = 4\mu \langle \rho_i \rho_k \rangle = \delta_{ik} + 2(f_1 + if_2)\tau^* \gamma_{ik}(t).$$

For the subchain model:

$$f_1 = \frac{6}{N^2} \sum_{\nu=1}^{N} \left[ \frac{p_1 R}{1+(xp_1)^2} + \frac{p_2 F}{1+(xp_2)^2} + \frac{p_3 G}{1+(xp_3)^2} \right],$$

$$f_2 = \frac{6x}{N^2} \sum_{\nu=1}^{N} \left[ \frac{p_1^2 R}{1+(xp_1)^2} + \frac{p_2^2 F}{1+(xp_2)^2} + \frac{p_3^2 G}{1+(xp_3)^2} \right], \tag{5}$$

where

$$p_1 = 2k(1+\sqrt{1-p}); \quad p_2 = kp; \quad p_3 = 2k(1-\sqrt{1-p}),$$

and for dumbbells:

$$f_1 = \frac{\theta}{1+(\theta x)^2(1+\gamma)^2} \left[ 1 + \frac{3}{5}\gamma(2+\gamma)\frac{(\theta x)^2}{1+(\theta x)^2} \right],$$

$$f_2 = \frac{\theta^2 x}{1+(\theta x)^2(1+\gamma)^2} \left[ 1 + \gamma - \frac{3}{5}\gamma \frac{1-(1+\gamma)(\theta x)^2}{1+(\theta x)^2} \right], \tag{6}$$

$$\theta = \tau_D/\tau^*, \quad \gamma = \lambda/\zeta, \quad x = \omega\tau^*.$$

For slow motions we separate Eqs. (5) and (6) according to frequency, and by equating the coefficients of the zero and first powers of x we obtain the relations:

$$\theta = \frac{6}{N^2} \sum_{\nu=1}^{N} (p_1 R + p_2 F + p_3 G), \tag{7}$$

$$\theta^2 \left( 1 + \frac{2}{5} \gamma \right) = \frac{6}{N^2} \sum_{\nu=1}^{N} (p_1^2 R + p_2^2 F + p_3^2 G). \tag{8}$$

Replacing the summation by an integration, we find for $B \gg 1$ and $\chi \ll 1$:

$$\tau_D = 2B\tau^* \left[ \frac{3}{\pi} \left( \frac{\chi}{1+\psi} \right)^{1,5} - \frac{\chi}{1+\psi} + \frac{\pi^2}{15} \right], \tag{9}$$

$$\gamma = \frac{\pi^4 (1+\psi)}{63 \left[ \frac{3}{\pi} \left( \frac{\chi}{1+\psi} \right)^{1,5} - \frac{\chi}{1+\psi} + \frac{\pi^2}{15} \right]^2}. \tag{10}$$

Since $\psi \gg 1$ for systems of high-molecular-weight polymers,

$$\tau_D = \frac{2\pi^2}{15} B\tau^*, \quad \gamma \gg 1. \tag{11}$$

It was shown in [4] that the approximation of a single relaxation time can be used to derive the expression $\tau = 2B\tau^*\chi$, which is $\chi$ times larger ($\chi \ll 1$) than the value given by (11). This result shows the inadequacy of the assumption of the correspondence of a dumbbell to a coiled macromolecule. Hence it follows that in the application to the systems under study a structural element of the medium being compared with a dumbbell is an appreciably smaller part of a macromolecule which can be identified with a chain within the limits of a characteristic length whose square is $\xi^2 \approx \langle L^2 \rangle \chi$.

4. Thus, for concentrated systems of macromolecules with a high molecular weight, the analysis presented makes it possible to specify a concrete form of the controlling equations. The relaxation time of the system is determined in terms of characteristics relating to a macromolecule. The value of the coefficient of internal viscosity $\gamma$ remains indeterminate: If a structural element of the flow were a coiled macromolecule, $\gamma \gg 1$, but this is not so, and therefore it is necessary to assume $\gamma \ll 1$, since internal viscosity does not play a substantial role on a small scale. In this case the controlling relations, Eqs. (1)-(3), are simplified. For $\gamma = 0$ they take the form

$$\sigma_{ij} = -p\delta_{ij} + 2\eta_E \gamma_{ij} + 3nT \frac{\langle L^2 \rangle}{\xi^2} \left( \langle \rho_i \rho_j \rangle - \frac{1}{3} \xi^2 \delta_{ij} \right), \tag{12}$$

$$\frac{d \langle \rho_i \rho_j \rangle}{dt} = -\frac{1}{\tau} \left( \langle \rho_i \rho_j \rangle - \frac{1}{3} \xi^2 \delta_{ij} \right) + \nu_{is} \langle \rho_s \rho_j \rangle + \nu_{js} \langle \rho_s \rho_i \rangle . \tag{13}$$

The system of equations is closed, which facilitates further analysis.

For simple shear ($\nu_{12} \neq 0$) Eqs. (12) and (13) (omitting the term with $\eta_E$) determine the viscosity $\eta$ and the difference of the normal stresses:

$$\sigma_{12} = \eta \nu_{12}, \quad \eta = nT \langle L^2 \rangle \tau, \tag{14}$$

$$\sigma_{11} - \sigma_{33} = \frac{2}{nT \langle L^2 \rangle} \sigma_{12}^2, \tag{15}$$

$$\sigma_{22} - \sigma_{33} = 0. \tag{16}$$

In the discussion of the relations obtained it is necessary to take account of the fact that the coefficient of friction $\zeta$ of a bead in terms of viscosity depends on a scalar parameter of state of the system of the type of free volume, and consequently depends on the secondary stress tensor $\sigma_{ij} = p\delta_{ij}$. From the definition of the coefficient of viscosity (14) we have

$$\frac{\eta}{\tau} = \frac{\eta_0}{\tau_0} = nT\langle L^2\rangle, \quad \frac{\eta}{\eta_0} = \frac{\tau}{\tau_0} = f(\sigma_{ij} + p\delta_{ij}). \tag{17}$$

The system of controlling equations (12), (13), and (17) is the simplest system which follows from current physical concepts of the structure and behavior of polymers, and was discussed in [3].

We note that by simplifying model (12), (13), (17) we obtain familiar models. Thus, if the function $f(\sigma_{ij} + p\delta_{ij})$ in (17) is constant, Eqs. (12) and (13) describe the Oldroyd model. By omitting the nonlinear terms in (13) we obtain the Maxwell model, and finally, for $\tau \to 0$ we obtain a Newtonian incompressible liquid. In spite of the general agreement of the results determined by Eqs. (12), (13), and (17), the experimental data, even for some simple cases [3], exhibit a number of effects, for example $\sigma_{22} - \sigma_{33} = 0$, which are not described by the equations listed above. This shows the necessity of taking account of internal viscosity, the hydrodynamic interaction, and the anisotropy of the internal medium in the model being considered for a more accurate formulation of the rheological relations. It should be noted that with the introduction of the indicated corrections, the system of equations is not generally closed, as in the case which takes account of internal viscosity (cf. Eqs. (1)-(3)). This gives an objective basis for the existence of different controlling equations based on various approximations for the same polymeric system. However, all models suitable for describing concentrated solutions of linear polymers must upon simplification reduce to Eqs. (12), (13) and (17). With this understanding, the system given above is the basis for the analysis of flows of linear polymers.

## NOTATION

$\sigma_{ik}$, stress tensor; p, pressure; $\delta_{ik}$, Kronecker symbol; $\eta_E$, coefficient of viscosity; $\nu_{ik}$, velocity gradient tensor; $\gamma_{ik}$, $\omega_{ik}$, symmetrized and antisymmetrized velocity gradient tensors; n, dumbbell number density; $\zeta$, coefficient of friction of Brownian bead-particle in viscous fluid; $\rho_i$, i-th component of normal coordinate of dumbbell; $\rho_i^\nu$, i-th component of $\nu$-th normal coordinate of subchain; $e_i$, component of unit vector along line connecting dumbbell beads; $\lambda$, coefficient of internal viscosity of dumbbell; t, time; $\tau_D = \zeta/8T\mu$ and $\tau' = (\lambda + \zeta)\tau/\zeta$, characteristic relaxation times of dumbbell; T, temperature; $2T\mu$, coefficient of elasticity of dumbbell; $2T\mu'$, coefficient of elasticity of subchain; m, mass of Brownian bead-particle; $\alpha_\nu$, eigenvalues of matrix of elastic interaction between three neighboring beads in a chain; $\Phi_i^\gamma$, random force; $R_{\gamma\nu}$, transformation matrix to normal coordinates; $\beta_\nu(s)$ and $\phi_\nu(s)$, functions characterizing external and "internal" viscosity of a macromolecule; $\langle L^2\rangle$, rms distance between ends of a macromolecule; $\tau$, relaxation time of viscoelastic medium; $\tau^*$, characteristic relaxation time; $\theta$, dimensionless relaxation time of dumbbell; $\chi$, dimensionless relaxation time of medium; B, measure of increase of coefficient of friction of bead as a result of involvement of surrounding macromolecules in the motion; E, measure of the "intramolecular" viscosity; $\psi$, measure of the kinetic rigidity of subchains; $\omega$, frequency of oscillating shear flow; x, dimensionless frequency; $\gamma$, parameter characterizing ratio of internal and external viscosities of dumbbell; (N + 1), number of subchains modelling a macromolecule; $\delta(s)$, delta function; $\langle S^2\rangle_0$, equilibrium value of rms radius of gyration tensor of a macromolecule; $\xi$, characteristic chain length.

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