GOVERNING EQUATION OF POLYMER SOLUTIONS ON THE BASIS OF THE DYNAMICS OF NONINTERACTING RELAXATION OSCILLATORS

Yu. A. Altukhov

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Special attention is currently being given to the study of systems formed by relatively large molecules (molecular liquids, liquid crystals, polymer solutions, etc.) in connection with different applications. A phenomenological approach proves inadequate in these cases: the nonlinear governing equations of the system are ambiguous and, no less important, the relationship between macroscopic effects and the internal characteristics of the system remains unclear. These questions are also studied by another approach, in which the structural units of the system are replaced by a suitable model. As is known, the simplest model of a macromolecule being deformed is a dumbbell – a relaxation oscillator with two centers of friction coupled by an elastic force. Such a model makes it possible to describe the basic features of the nonlinear behavior of polymer solutions [1, 2]. The goal of the present work is to derive governing equations with allowance for the hydrodynamic interaction of the friction centers of the relaxation oscillators. This approach leads to the most general form of governing equation of a dilute polymer solution, while allowance for hydrodynamic interaction leads to the discovery of new effects in the study of simple shear flow. For example, the second difference of the normal stresses is nontrivial.

1. Dynamics of a Relaxation Oscillator in a Flow. We will examine the behavior of a macromolecule represented by a dumbbell – two Brownian particles with the coordinates r', r'' and velocities w', w'' coupled by elastic forces and located in a flow of a viscous fluid with an asymptotically prescribed velocity gradient ν_{ij}.

The first particle, with the radius vector r', is acted upon by the elastic force

$$-2T\mu(\mathbf{r}' - \mathbf{r}'') \quad (1.1)$$

(T is the temperature), the hydrodynamic resistance

$$B_{ki}^{11}\left(\nu_{ij}r_j' - w_i'\right) + B_{ki}^{12}\left(\nu_{kj}r_j'' - w_i''\right), \quad (1.2)$$

the force associated with internal viscosity, which according to Kuhn [1] has the form

$$\frac{1}{2}\lambda e_i e_j\left(w_j'' - w_j'\right), \quad e_i = \frac{r_i'' - r_i'}{|\mathbf{r}'' - \mathbf{r}'|}, \quad (1.3)$$

and a random force expressed through the distribution function W(r', r'', t),

$$-T\frac{\partial \ln W}{\partial r_i'}. \quad (1.4)$$

If we interchange the superscripts ' and '' in the above expressions, we obtain expressions for the forces acting on the second particle.

When the mutual effect of the spheres of the dumbbell is slight, the matrix of hydrodynamic resistance $B_{ij}^{\alpha\beta}$ can be written [3] in the Ozeen approximation

$$B_{ij}^{11} = B_{ij}^{22} = \frac{\zeta}{1 - L^2}\delta_{ij} + \frac{3\zeta L^2}{(1 - L^2)(1 - 4L^2)}e_i e_j \simeq \zeta(1 + L^2)\delta_{ij} + 3\zeta L^2 e_i e_j,$$

$$B_{ij}^{12} = B_{ij}^{21} = -\frac{\zeta L}{1 - L^2}\delta_{ij} - \frac{\zeta L(1 + 2L^2)}{(1 - L^2)(1 - 4L^2)}e_i e_j \simeq -\zeta L\delta_{ij} - \zeta L e_i e_j,$$

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where $\zeta = 6\pi R\eta_0$ is the friction coefficient of a sphere of radius R in a liquid with the shear viscosity coefficient η_0;

$$L = \frac{\zeta}{8\pi\eta_0 |\mathbf{r}'' - \mathbf{r}'|} = \frac{3R}{4|\mathbf{r}'' - \mathbf{r}'|} = \frac{a}{|\mathbf{r}'' - \mathbf{r}'|} \ll 1.$$

Forces (1.1-1.4) determine the motion of the dumbbell in the fluid flow.

It is now convenient to introduce the coordinates and velocities

$$\rho_i^0 = \frac{1}{\sqrt{2}}(r_i'' + r_i'), \quad \rho_i = \frac{1}{\sqrt{2}}(r_i'' - r_i'),$$
$$\psi_i^0 = \frac{1}{\sqrt{2}}(w_i'' + w_i'), \quad \psi_i = \frac{1}{\sqrt{2}}(w_i'' - w_i').$$

Without allowance for inertial forces − which are small in the case being examined − the equations of motion of the relaxation oscillator (dumbbell) have the following form in the new coordinates

$$4T\mu\rho_i - B_{ij}^{11}[\psi_j^0 - \psi_j + \nu_{jl}(\rho_l - \rho_l^0)] - B_{ij}^{12}[\psi_j^0 + \psi_j - \nu_{jl}(\rho_l + \rho_l^0)] + \lambda e_i e_j \psi_j - T\left(\frac{\partial}{\partial\rho_i^0} - \frac{\partial}{\partial\rho_i}\right)\ln W = 0; \quad (1.5)$$

$$-4T\mu\rho_i - B_{ij}^{21}[\psi_j^0 - \psi_j + \nu_{jl}(\rho_l - \rho_l^0)] - B_{ij}^{22}[\psi_j^0 + \psi_j - \nu_{jl}(\rho_l + \rho_l^0)] - \lambda e_i e_j \psi_j - T\left(\frac{\partial}{\partial\rho_j^0} + \frac{\partial}{\partial\rho_j}\right)\ln W = 0. \quad (1.6)$$

Equations (1.5-1.6) describe the rate of diffusion of the center of mass ψ^0 and the rate of diffusion of the spheres of the dumbbell relative to each other ψ.

To within second-order terms for L, the following equation, obtained from Eqs. (1.5) and (1.6), describes ψ_i

$$\psi_i = \nu_{il}\rho_l - \frac{T}{\zeta}\nabla_i \ln W - \frac{\lambda}{\lambda+\zeta}\nu_{jl}e_l e_j \rho_i + \frac{T\lambda}{\zeta(\lambda+\zeta)} e_i e_j \nabla_j \ln W \quad (1.7)$$
$$- \frac{4T\mu}{\lambda+\zeta}\rho_i + \frac{TL}{\zeta}\nabla_i \ln W + \frac{2\lambda\zeta L}{(\lambda+\zeta)^2}\nu_{jl}e_l e_j \rho_i + ALe_i e_j \nabla_j \ln W +$$
$$+ \frac{8T\mu\zeta}{(\lambda+\zeta)^2}L\rho_i + \frac{4\zeta\lambda^2}{(\lambda+\zeta)^3}L^2\nu_{jl}e_l e_j \rho_i + \frac{4\zeta\lambda T}{(\lambda+\zeta)^3}L^2 e_i e_j \nabla_j \ln W + \frac{16T\mu\zeta\lambda}{(\lambda+\zeta)^3}L^2\rho_i.$$

Here $\nabla_i = \frac{\partial}{\partial\rho_i}$; $A = \frac{\zeta^2 - 2\lambda\zeta - \lambda^2}{\zeta(\lambda+\zeta)^2}T$.

Now the equation for the distribution function $W(\rho, t)$ [4] has the form

$$\frac{\partial W}{\partial t} + \frac{\partial(\psi_j W)}{\partial\rho_j} = 0. \quad (1.8)$$

To within second-order terms for the velocity gradients and first-order terms for $\gamma^{-1} = \zeta/\lambda$, the following function is obtained as the solution of Eq. (1.8) in the steady-state case

$$W_0(\rho) = \left(\frac{2\mu}{\pi}\right)^{3/2}\exp(-2\mu\rho^2)\left\{1 + \frac{\zeta}{T}\gamma_{lm}\rho_l\rho_m + \frac{1}{8}\left(\frac{\zeta}{T}\right)^2\gamma_{lm}\gamma_{sj}\rho_l\rho_m\rho_s\rho_j\right.$$
$$\left. - \tau^2\gamma_{lm}\gamma_{lm} - \left[\frac{1}{6}\rho^2 + \frac{1}{9}\frac{\rho^2}{\gamma}(5 - 4\mu\rho^2)\right]\left(\frac{\zeta}{T}\right)^2\gamma_{sl}\omega_{sm}\rho_l\rho_m\right\},$$

where $\tau = \zeta/(6T\mu)$; γ_{lm}, ω_{lm} are symmetrical and antisymmetrical tensors of the velocity gradients.

We now need to know the moments of the distribution function, such as the second-order moments

$$\langle\rho_i\rho_k\rangle = \int_{-\infty}^{\infty} W(\rho, t)\rho_i\rho_k\{d\rho\},$$

through which we express the macroscopic properties of the system.

2. Governing Equations. The stress tensor of the suspension of Brownian particles σ_{ik} being examined is expressed through the moments of the distribution function as follows [4]:

$$\sigma_{ik} = -nT\delta_{ik} + n[-T\delta_{ik} + 4T\mu\langle\rho_i\rho_k\rangle + \lambda\langle e_ie_k\psi_j\rho_j\rangle] \tag{2.1}$$

(n is the density of the number of macromolecules).

This expression must be augmented by the stress tensor of the carrying medium

$$\sigma^0_{ik} = -p^0\delta_{ik} + 2\eta_e\gamma_{ik},$$

where p^0 is the partial pressure of the solvent; η_e is the viscosity coefficient of the carrying medium.

Using the expression for the elative rate of diffusion of particles of the relaxation oscillator (1.7) and performing the necessary transformation, we find the following expression, accurate to within the second-order terms for a

$$\sigma_{ik} = -nT\delta_{ik} + \frac{1}{2}n\zeta\left[\frac{1}{\tau'}\left(\langle\rho_i\rho_k\rangle - \frac{3}{4\mu}\langle e_ie_k\rangle + \frac{1}{\tau}\frac{3}{4\mu}\left(\langle e_ie_k\rangle - \frac{1}{3}\delta_{ik}\right) + \frac{2\lambda}{\lambda+\zeta}\langle\rho_i\rho_ke_je_s\rangle\gamma_{js}\right] + \tag{2.2}$$

$$+ na\lambda\left[-\frac{1}{4\mu\tau}\left(1+\frac{A}{T}\right)\left\langle\frac{e_ie_k}{\rho}\right\rangle + \frac{1}{\tau'}\frac{\zeta}{\lambda+\zeta}\left\langle\frac{\rho_i\rho_k}{\rho}\right\rangle + \frac{2\lambda\zeta}{(\lambda+\zeta)^2}\gamma_{ml}\langle e_le_me_i\rho_k\rangle\right] + na^2\left[\frac{4\zeta\lambda^3}{(\lambda+\zeta)^3}v_{ml}\langle e_ie_ke_me_l\rangle - \right.$$

$$\left. - \frac{4\zeta\lambda^2T}{(\lambda+\zeta)^3}\left\langle\frac{e_ie_k}{\rho^2}\right\rangle + \frac{16T\mu\zeta\lambda}{(\lambda+\zeta)^3}\langle e_ie_k\rangle\right].$$

Here, τ and $\tau' = [(\lambda + \zeta)/\zeta]\tau$ are characteristic times of the relaxation processes.

To find an equation for the moments, we multiply (1.8) by $\rho_i\rho_k$ and integrate over all of the variables with allowance for (1.7) to obtain

$$\frac{d\langle\rho_i\rho_k\rangle}{dt} = -\frac{1}{\tau}\frac{3}{4\mu}\left(\langle e_ie_k\rangle - \frac{1}{3}\delta_{ik}\right) - \frac{1}{\tau'}\left(\langle\rho_i\rho_k\rangle - \frac{3}{4\mu}\langle e_ie_k\rangle\right) + v_{ij}\langle\rho_j\rho_k\rangle + v_{kj}\langle\rho_j\rho_i\rangle - \frac{2\gamma}{1+\gamma}\langle\rho_i\rho_ke_le_m\rangle\gamma_{lm} \tag{2.3}$$

$$-\frac{a}{4\mu\tau}\left(\delta_{ik}\left\langle\frac{1}{\rho}\right\rangle - \left\langle\frac{e_ie_k}{\rho}\right\rangle\right) + \frac{a}{2\mu\tau}\left(1 - \frac{2}{(1+\gamma)^2}\right)\left\langle\frac{e_ie_k}{\rho}\right\rangle$$

$$+ \frac{4a\gamma}{(1+\gamma)^2}\langle\rho_ie_ke_le_m\rangle\gamma_{lm} + \frac{2a}{\tau(1+\gamma)^2}\left\langle\frac{\rho_i\rho_k}{\rho}\right\rangle + \frac{8a^2\gamma^2}{(1+\gamma)^3}\langle e_ie_ke_le_m\rangle\gamma_{lm} - \frac{a^2\gamma}{\mu\tau(1+\gamma)^3}\left\langle\frac{e_ie_k}{\rho^2}\right\rangle + \frac{4a^2}{\tau\zeta(1+\gamma)^3}\langle e_ie_k\rangle.$$

When the characteristic times of motion are significantly greater than the relaxation times, the stress tensor (2.2), with allowance for (2.3), takes the following form

$$\sigma_{ik} = -nT\delta_{ik} + \frac{1}{2}n\zeta[v_{ij}\langle\rho_j\rho_k\rangle + v_{kj}\langle\rho_j\rho_i\rangle] \tag{2.4}$$

$$+ an\zeta\left[-\frac{\delta_{ik}}{8\mu\tau}\left\langle\frac{1}{\rho}\right\rangle + \frac{1}{\tau'}\left\langle\frac{\rho_i\rho_k}{\rho}\right\rangle + \frac{1}{4\mu\tau}\left(\frac{1}{2}+\frac{\gamma-1}{\gamma+1}\right)\left\langle\frac{e_ie_k}{\rho}\right\rangle + \frac{2\gamma}{1+\gamma}\langle\rho_ie_ke_le_m\rangle\gamma_{lm}\right] + n\zeta a^2\left\{4\frac{\gamma^2}{(1+\gamma)^3}\gamma_{ml}\langle e_ie_ke_le_m\rangle\right.$$

$$\left. + 4\frac{\gamma^3}{(1+\gamma)^3}v_{ml}\langle e_ke_ie_le_m\rangle - \frac{1}{2\mu\tau}\frac{\gamma(1+\gamma^2)}{(1+\gamma)^3}\left\langle\frac{e_ie_k}{\rho^2}\right\rangle + \frac{2}{\zeta(1+\gamma)^2}\langle e_ie_k\rangle\right\}.$$

Calculating the moments in Eq. (2.4) with the necessary accuracy and using the above form of the function $W_0(\rho)$, we find the stress tensor to within second-order terms for the velocity gradients and a:

$$\sigma_{ik} = -nT\delta_{ik} + \frac{1}{2}n\zeta\left\{\frac{1}{2\mu}\gamma_{ik} + \tau(v_{ij}\gamma_{jk} + v_{kj}\gamma_{ji})\left[\frac{1}{2\mu}\right.\right. \tag{2.5}$$

$$\left.\left. + \left(\frac{16a^2\gamma}{15(1+\gamma)} - \frac{1}{5\mu\gamma}\right)\right]\right\} + na^2\zeta\left\{\frac{4\gamma^3}{(1+\gamma)^3}\left[\frac{2}{15}(v_{ik} + \gamma^{-1}\gamma_{ik}) + \right.\right.$$

$$+\frac{2\tau}{35}(\gamma^{-1}\delta_{ik}\gamma_{ml}\gamma_{ml}+4\gamma^{-1}\gamma_{il}\gamma_{lk}+\delta_{ik}\nu_{ml}\gamma_{ml}+\gamma_{km}\nu_{mi}+\gamma_{im}\nu_{mk}+\nu_{kl}\gamma_{li}+$$

$$\nu_{il}\gamma_{lk})]-\frac{1}{2\mu\tau}\frac{\gamma^3}{(1+\gamma)^3}\left[\frac{4}{3}\mu\delta_{ik}+\frac{8}{15}\mu\tau\gamma_{ik}-\frac{128}{105}\mu\tau^2\delta_{ik}\gamma_{lm}\gamma_{lm}+\frac{16}{35}\mu\tau^2\gamma_{is}\gamma_{sk}+\frac{8}{15}\mu\tau^2(\omega_{ks}\gamma_{si}+\omega_{is}\gamma_{sk})\right]\Big\}.$$

Besides the symmetrized tensor, the antisymmetrized tensor also determines the stress tensor due to the presence of internal parameters — the moments.

3. Conclusion. Thus, the governing equations of a dilute polymer solution consist of the stress tensor (2.1) and the system of equations for the moments. We should point out that, considering the internal viscosity of the macromolecules and the mutual hydrodynamic effect of the molecules, the governing equations do not constitute a closed system in the case of an arbitrary flow: the lowest-order moments are expressed through higher-order moments. However, a different approximation, permitting closure of the system for the moments, may be possible, depending on the problem being examined. This realization provides objective grounds for the argument that different governing equations exist for polymer solutions.

We will examine a simple stationary shear flow $\nu_{12} \neq 0$. In contrast to the case studied in [4], allowance for hydrodynamic interaction and internal viscosity leads to a qualitatively new effect. In fact, using Eqs. (2.1) and (2.5), we write the shear stress and the difference in the normal stresses in the form

$$\sigma_{11}-\sigma_{33}=2nT(\tau\nu_{12})^2\left(1+\frac{32}{15}\frac{a^2\mu\gamma}{(1+\gamma)^3}-\frac{2}{5}\gamma^{-1}\right)+\frac{na^2\zeta}{\tau}(\tau\nu_{12})^2\frac{\gamma^3}{(1+\gamma)^3}\left(\frac{4}{105}+\frac{8}{35}\gamma^{-1}\right),$$

$$\sigma_{22}-\sigma_{33}=\frac{na^2\zeta}{\tau}\frac{\gamma^3(\tau\nu_{12})^2}{(1+\gamma)^3}\left(-\frac{41}{105}+\frac{8}{35}\gamma^{-1}\right),$$

$$\sigma_{12}=\eta\nu_{12},\quad \eta=\eta_H+nT\tau+8a^2\mu T\tau\frac{\gamma^3}{(1+\gamma)^3}\left(\frac{2}{5}+\frac{4}{15}\gamma^{-1}\right),$$

from which it is evident that the additive terms in the expressions for the stresses in the suspension are determined by the parameters of internal viscosity γ and hydrodynamic interaction $a^2\mu$. The expression for the second difference in the normal stresses is of particular interest. This quantity is nontrivial only when internal viscosity and the anisotropy of the hydrodynamic interaction are nontrivial. Its measurement makes it possible to quantitatively evaluate the anisotropy of the interaction. The use of a more current model of the macromolecule — the subchain model, in which the macromolecule is modeled by a chain of many Brownian particles [5] — does not alter the conclusions reached here because each normal coordinate of the subchain model is equivalent to a dumbbell, the parameters of which are dependent on the number of the normal coordinate.

Thus, it can be assumed that the form of the governing equations presented here is the most general form of these equations for dilute polymer solutions. There is one more significant factor to be considered for concentrated polymer solutions when formualting the governing equations: the interaction of the macromolecules within the framework of the relaxation oscillator model.

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