RHEOLOGICAL EQUATIONS OF STATE OF WEAK SOLUTIONS OF POLYMERS AS RIGID ELLIPSOIDAL MACROMOLECULES

Yu. V. Pridatchenko and Yu. I. Shmakov

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Rheological equations of state are obtained for weak solutions of polymers as rigid ellipsoidal macromolecules, taking into account the rotational Brownian motion of the macromolecules, their energy, and the external force fields (electric and magnetic). As an example the effect of the inertia of the macromolecules on the rheological behavior of the solutions is examined.

In recent years a number of phenomenological theories have appeared in rheology which have received the name of structural continuum theory. In them attempts are made to account for the structural properties of a medium by introducing one or several parameters into the equation of state, with the help of which one can describe the behavior of the structure (orientation, deformation, interaction of substructure elements) [1-6].

A structural-continuum approach, incorporating the results obtained from the position of macro- and microrheology, was proposed in [7] for the construction of rheological equations of state of weak solutions of polymers, the macromolecules of which could be simulated by relatively simple geometrical bodies. Rheological equations of state are obtained for weak solutions of polymers, for which a rigid ellipsoid of rotation can serve as the macromolecule model, taking the Brownian motion of the latter into account.

The results of [7] are generalized below taking into account the inertia of the macromolecules and the effect of external force fields.

We shall examine the determining equations of an incompressible anisotropic liquid [6] for isothermal flow with a fixed length of the vector n_i characterizing the substructure behavior (the orientation, in the case under examination):

$$t_{ij}=(a_0+a_1d_{km}n_kn_m)\delta_{ij}+a_2n_in_j+a_3d_{km}n_kn_mn_in_j+a_4d_{ij}+a_5d_{ik}n_kn_j+a_6d_{jk}n_kn_i+a_7n_iN_j+a_8n_jN_i \qquad (1)$$

$$\dot{n}_i=\gamma\,[N_i-\lambda\,(d_{ij}n_j-d_{jk}n_jn_kn_i)]+\delta n_i \qquad (2)$$

where t_{ij} is the tensor of the stresses, $N_i=\dot{n}_i-\omega_{ij}n_j$, d_{ij} is the tensor of the rates of deformation, ω_{ij} is the vortex tensor, γ, λ, δ, a_k ($k=0, 1, \ldots, 8$) are rheological constants, and δ_{ij} is the Kronecker symbol.

The rheological constants in Eq. (1) can be determined with the help of the results obtained by Jeffery [8], which detected disturbances introduced into the flow of a viscous Newtonian liquid by a rigid ellipsoid suspended in it. Knowing these disturbances, we find the tensor of the stresses σ_{ij} at the surface of a sphere, the center of which coincides with the center of the suspended particle, while the radius R considerably exceeds its dimensions. In a moving system of coordinates x_i with the origin at the center of the particle and with axes directed along the main axes of the ellipsoid of rotation corresponding to the shape of the particle, we obtain

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$$\sigma_{ij} = -p\delta_{ij} + 2\mu d_{ij} + 10\mu\left(\frac{5}{R^5}\Phi\delta_{ij} + \frac{4x_i x_j}{R^7}\Phi - \frac{x_i}{R^5}\frac{\partial\Phi}{\partial x_i} - \frac{x_j}{R^5}\frac{\partial\Phi}{\partial x_i}\right) \tag{3}$$

$$\Phi = A_{km}x_k x_m$$

$$A_{11} = \frac{d_{11}}{6\beta_0''}, \quad A_{12} = \frac{\alpha_0 d_{12} + b^2\beta_0'(\omega_{12} + \omega_3)}{2\beta_0' B}$$

$$A_{13} = \frac{\alpha_0 d_{13} + b^2\beta_0'(\omega_{13} - \omega_2)}{2\beta_0' B}, \quad A_{21} = \frac{\beta_0 d_{21} + a^2\beta_0'(\omega_{21} - \omega_3)}{2\beta_0' B}$$

$$A_{22} = \frac{d_{22}}{4b^2\alpha_0'} + \frac{d_{11}(\beta_0'' - \alpha_0'')}{12b^2\beta_0''\alpha_0'}, \quad A_{23} = \frac{d_{23}}{4b^2\alpha_0'}$$

$$A_{31} = \frac{\beta_0 d_{31} + a^2\beta_0'(\omega_{31} + \omega_2)}{2\beta_0' B}, \quad A_{32} = \frac{d_{32}}{4b^2\alpha_0'}$$

$$A_{33} = \frac{d_{33}}{4b^2\alpha_0'} + \frac{d_{11}(\beta_0'' - \alpha_0'')}{12b^2\beta_0''\alpha_0'}$$

$$B = a^2\alpha_0 + b^2\beta_0$$

where $2a$ and b are the axis of rotation and the equatorial radius of the ellipsoidal particle, respectively, p is the pressure, μ is the dynamic coefficient of viscosity of the solvent, the values α_0, β_0, α_0', β_0', α_0'', and β_0'' are determined in [8], and ω_2 and ω_3 are components of the angular velocity of rotation of the ellipsoidal particle.

As the stress tensor describing the state of stress in the solution we use the average of the stress tensor σ_{ij} over the volume of the sphere under consideration, which we find by a conversion from the integral over the volume of the sphere to an integral over its surface [9]:

$$\begin{aligned}
\langle\sigma_{11}\rangle &= -p + \left(2\mu + \frac{4\mu V}{3ab^2\beta_0''}\right)d_{11} \\
\langle\sigma_{22}\rangle &= -p + \left(2\mu + \frac{2\mu V}{ab^4\alpha_0'}\right)d_{22} + \frac{2\mu V(\beta_0'' - \alpha_0'')}{3ab^4\beta_0''\alpha_0'}d_{11} \\
\langle\sigma_{33}\rangle &= -p + \left(2\mu + \frac{2\mu V}{ab^4\alpha_0'}\right)d_{33} + \frac{2\mu V(\beta_0'' - \alpha_0'')}{3ab^4\beta_0''\alpha_0'}d_{11} \\
\langle\sigma_{12}\rangle &= \left(2\mu + \frac{4\mu\alpha_0 V}{ab^2\beta_0' B}d_{12}\right) + \frac{4\mu V b^2(\omega_{12} + \omega_3)}{ab^2 B} \\
\langle\sigma_{21}\rangle &= \left(2\mu + \frac{4\mu\beta_0 V}{ab^2\beta_0' B}\right)d_{21} + \frac{4\mu V a^2(\omega_{21} - \omega_3)}{ab^2 B} \\
\langle\sigma_{13}\rangle &= \left(2\mu + \frac{4\mu\alpha_0 V}{ab^2\beta_0' B}\right)d_{13} + \frac{4\mu V b^2(\omega_{13} - \omega_2)}{ab^2 B} \\
\langle\sigma_{31}\rangle &= \left(2\mu + \frac{4\mu\beta_0 V}{ab^2\beta_0' B}\right)d_{31} + \frac{4\mu V a^2(\omega_{31} + \omega_2)}{ab^2 B} \\
\langle\sigma_{23}\rangle &= \left(2\mu + \frac{2\mu V}{ab^4\alpha_0'}\right)d_{23} \\
\langle\sigma_{32}\rangle &= \left(2\mu + \frac{2\mu V}{ab^4\alpha_0'}\right)d_{32}
\end{aligned} \tag{4}$$

where V is the volumetric concentration of the suspended particles.

We shall consider the function (1) in the moving system of coordinates x_i, taking as the vector n_i the unit vector directed along the axis of rotation of the ellipsoidal particle. Then $n_1 = 1$, $n_2 = 0$, $n_3 = 0$, $\dot{n}_1 = 0$, $\dot{n}_2 = \omega_3$, $\dot{n}_3 = -\omega_2$, and the components of the stress tensor $\{t_{ij}\}$ in (1) take the form

$$\begin{aligned}
t_{11} &= a_0 + a_1 d_{11} + a_2 + (a_3 + a_4 + a_5 + a_6)\,d_{11} \\
t_{22} &= a_0 + a_1 d_{11} + a_4 d_{22}, \quad t_{33} = a_0 + a_1 d_{11} + a_4 d_{33} \\
t_{12} &= (a_4 + a_6)\,d_{12} + a_7(\omega_3 + \omega_{12}) \\
t_{21} &= (a_4 + a_5)d_{21} + a_8(\omega_3 - \omega_{21}) \\
t_{13} &= (a_4 + a_6)\,d_{13} + a_7(-\omega_2 + \omega_{13}) \\
t_{31} &= (a_4 + a_5)\,d_{31} + a_8(-\omega_2 - \omega_{31}) \\
t_{23} &= a_4 d_{23}, \quad t_{32} = a_4 d_{32}
\end{aligned} \tag{5}$$

Comparing (4) and (5), we obtain

$$a_0 = -p, \ a_1 = \frac{2\mu V(\beta_0'' - \alpha_0'')}{3ab^4\beta_0''\alpha_0'}, \quad a_3 = \frac{2\mu V}{ab^2}\left[\frac{\alpha_0'' + \beta_0''}{b^2\alpha_0'\beta_0''} - \frac{2(\alpha_0 + \beta_0)}{\beta_0' B}\right]$$

$$a_4 = 2\mu\left(1 + \frac{V}{ab^4\alpha_0'}\right), \quad a_5 = \frac{4\mu V}{ab^2}\left(\frac{\beta_0}{\beta_0' B} - \frac{1}{2b^2\alpha_0'}\right) \tag{6}$$

$$a_6 = \frac{4\mu V}{ab^2}\left(\frac{\alpha_0}{\beta_0' B} - \frac{1}{2b^2\alpha_0'}\right), \quad a_7 = \frac{4b^2\mu V}{ab^2 B}, \ a_8 = -\frac{4a^2\mu V}{ab^2 B}$$

Thus, the constants a_k (k = 0, 1, 3, ..., 8) in Eq. (1) are determined up to an examination of the rotation of the suspended particles. In the comparison of (4) and (5) a_2 had to be set equal to 0, but by analogy with [7] we shall leave the value of a_2 indeterminant for now since in the present case the term of Eq. (1) containing a_2 can be used to calculate the rotational Brownian motion of the macromolecules.

In the general case, in addition to hydrodynamic forces, forces produced by rotational Brownian motion and by external force fields can act on the particle. In this case the orientation of the particle is characterized by distribution functions of the angular positions of the axis of rotation F of the ellipsoidal particle, which is determined from the equation [10]

$$\partial F / \partial t = Dr \Delta F - \operatorname{div}(F\Omega) \tag{7}$$

Here t is the time, Dr is the coefficient of rotational diffusion of the particle, Δ is the Laplace operator, and Ω is the angular velocity of the particle.

The equation of orientation for an ellipsoidal particle, neglecting the moment of inertia relative to the axis of rotation of the ellipsoid in the system of coordinates x_i, has the form

$$0 = M_1 + M_1^\circ, \quad I(\dot\omega_2 - \omega_1\omega_3) = M_2 + M_2^\circ, \quad I(\dot\omega_3 + \omega_1\omega_2) = M_3 + M_3^\circ \tag{8}$$

where I is the moment of inertia of the ellipsoid relative to an axis lying in its equatorial plane, ω_k (k = 1, 2, 3) are components of the angular velocity of the ellipsoid, M_k are components of the moment of the hydrodynamic forces, determined by Jeffery's method [8], and M_k° are components of the moment of forces produced by external fields and dependent on the properties of the particles and the external fields.

We note that in the absence of external force fields Eqs. (8) coincide with Eqs. (2) for the adopted interpretation of the vector n_i and a suitable form of the chosen rheological constants γ, λ, and δ.

As the rheological equations of state of weak solutions of polymers, the macromolecules of which can be simulated by a rigid ellipsoid of rotation, we take the expression for the stress tensor of an anisotropic liquid of Ericksen t_{ij} (1), averaged using the distribution function of F determined by Eqs. (7) and (8), with rheological constants a_k (k = 0, 1, 3, ..., 8) related to the substructure parameters by Eqs. (6):

$$T_{ij} = \langle t_{ij}\rangle = (a_0 + a_1 d_{km}\langle n_k n_m\rangle)\delta_{ij} + a_2\langle n_i n_j\rangle + a_3 d_{km}\langle n_k n_m n_i n_j\rangle + a_4 d_{ij} +$$
$$+ a_5 d_{ik}\langle n_k n_j\rangle + a_6 d_{jk}\langle n_k n_i\rangle + a_7\langle n_i N_j\rangle + a_8\langle n_j N_i\rangle \tag{9}$$

To determine the rheological constant a_2 we shall examine the particular case when the external force fields are absent and the inertia of the particles is negligibly small. Then the orientation equations have the form

$$M_1 = 0, \ M_2 = 0, \ M_3 = 0$$

and coincide with Ericksen's orientation equations of a simple anisotropic liquid [11]

$$N_i = \lambda(d_{ij}n_j - d_{kj}n_k n_j n_i) \tag{10}$$

for the chosen interpretation of the vector n_i and $\lambda = (a^2 - b^2)(a^2 + b^2)^{-1}$. The latter follows from the general expression $\lambda = (a_6 - a_5)(a_8 - a_7)^{-1}$ [6, 12] and Eqs. (6).

Substituting (10) into (9), we arrive in the present case at the rheological equations obtained in [7] for

$$a_2 = 12\mu Dr \frac{V}{ab^2}\frac{a^2 - b^2}{B} \tag{11}$$

We shall take the value of a_2 determined from Eq. (11) as the missing rheological constant.

As an example we shall examine Couette flow of a solution of polymers consisting of rigid ellipsoidal macromolecules in the absence of external force fields and neglecting rotational Brownian motion.

The equations of orientation have the form

$$M_1 = 0, \qquad I(\dot{\omega}_2 - \omega_1\omega_3) = M_2, \qquad I(\dot{\omega}_3 + \omega_1\omega_2) = M_3 \tag{12}$$

Substituting into (12) the values of the moment of inertia and the moments of the hydrodynamic forces computed by Jeffery [8] for simple transverse flow $V_x = 0$, $V_y = kx$, $V_z = 0$, where V_x, V_y, and V_z are the velocity components in the Descartes coordinate system xyz, and k = const, we obtain equations for the description of the orientation of an ellipsoidal particle:

$$\ddot{\theta} - \dot{\varphi}^2 \sin\theta\cos\theta = \gamma\left[\frac{\lambda k}{2}\sin\theta\cos\theta\sin 2\varphi - \dot{\theta}\right] \tag{13}$$

$$\ddot{\varphi}\sin\theta + 2\dot{\theta}\dot{\varphi}\cos\theta = \gamma\left[\frac{\lambda k}{2}\sin\theta\cos 2\varphi + \left(\frac{k}{2} - \dot{\varphi}\right)\sin\theta\right]$$

Here φ is the angle between the x axis and the projection of the axis of rotation of the ellipsoidal particle on the xy plane, θ is the angle between the z axis and the particle's rotation axis, m is the particle's mass, and

$$\gamma = \frac{80\pi\mu}{3mB}, \qquad \lambda = \frac{a^2 - b^2}{a^2 + b^2}$$

In the case of rotation of the macromolecules having been established in the plane of displacement ($\theta = \pi/2$), the quantity $\dot{\varphi}$ needed to determine the function F (7) will be sought in the form of an asymptotic expansion in powers of the small parameter k/γ.

Neglecting terms of order $(k/\gamma)^2$ and higher, we obtain

$$\dot{\varphi} = \frac{k}{2}(1 + \lambda\cos 2\varphi)\left(1 + \frac{\lambda k}{\gamma}\sin 2\varphi\right)$$

From Eq. (7) we find the distribution function

$$F(\varphi) = \frac{q}{\pi}(q^2+1)^{-1}(1 + \lambda\cos 2\varphi)^{-1}\left(1 + \frac{\lambda k}{\gamma}\sin 2\varphi\right)^{-1} \tag{14}$$

We determine the values $T_{11} - T_{33}$, $T_{22} - T_{33}$, $\frac{1}{2}(T_{12} + T_{21})$, $\frac{1}{2}(T_{12} - T_{21})$ and the averaged function for T_{ij} (9) using the distribution function (14):

$$T_{11} - T_{33} = a_3\langle\sin\varphi\cos^3\varphi\rangle k + (a_5 + a_6 + a_7 + a_8)\langle\sin\varphi\cos\varphi\rangle k/2 - (a_7 + a_8)\langle\dot{\varphi}\sin\varphi\cos\varphi\rangle$$

$$T_{22} - T_{33} = a_3\langle\sin^3\varphi\cos\varphi\rangle k + (a_5 + a_6 - a_7 - a_8)\langle\sin\varphi\cos\varphi\rangle k/2 + (a_7 + a_8)\langle\dot{\varphi}\sin\varphi\cos\varphi\rangle \tag{15}$$

$$\frac{T_{12} + T_{21}}{2} = \left[a_3\langle\sin^2\varphi\cos^2\varphi\rangle - \frac{a_7 + a_8}{4}\langle\cos 2\varphi\rangle + \frac{a_4 + a_5 + a_6}{2}\right]k + \frac{a_7 + a_8}{2}\langle\dot{\varphi}\cos 2\varphi\rangle$$

$$\frac{T_{12} - T_{21}}{2} = \frac{a_7 - a_8}{2}\left(\langle\dot{\varphi}\rangle - \frac{k}{2}\right) + \frac{a_6 - a_5}{2}\langle\cos 2\varphi\rangle\frac{k}{2}$$

Here

$$\langle\sin\varphi\cos^3\varphi\rangle = \frac{kq(q^3 - 4q^2 + q - 2)}{4\gamma(q+1)^2(q^2+1)}$$

$$\langle\sin^3\varphi\cos\varphi\rangle = -\frac{kq(q-1)(q^2+q+2)}{4\gamma(q+1)^2(q^2+1)} \tag{16}$$

$$\langle\sin\varphi\cos\varphi\rangle = -\frac{kq(q-1)}{\gamma(q+1)(q^2+1)}$$

$$\langle\sin^2\varphi\cos^2\varphi\rangle = \frac{q}{2(q+1)^2}, \qquad \langle\cos 2\varphi\rangle = -\frac{q-1}{q+1}$$

$$\langle\dot{\varphi}\rangle = \frac{kq}{q^2+1}, \qquad \langle\dot{\varphi}\sin\varphi\cos\varphi\rangle = \langle\dot{\varphi}\cos 2\varphi\rangle = 0$$

It follows from the functions (15) and (16) that in the case under consideration the stress tensor is symmetrical, the effective viscosity does not depend on the rate of displacement, and the differences in the normal stresses $T_{11}-T_{33}$ and $T_{22}-T_{33}$ differ from zero.

Thus, weak solutions of polymers, the macromolecules of which can be simulated by rigid ellipsoids of rotation taking into account the inertia of the macromolecules, exhibit non-Newtonian properties, even if the Brownian motion of the macromolecules is not considered [7].

LITERATURE CITED

1. S. J. Allen and C. N. DeSilva, "A theory of transversely isotropic fluids," J. Fluid Mech., 24, Part 4 (1966).
2. S. J. Allen, C. N. DeSilva, and K. A. Kline, "Theory of simple deformable directed fluids," Phys. Fluids, 10, No. 12 (1967).
3. K. A. Kline and S. J. Allen, "On continuum theories of suspensions of deformable particles," Z. Angew. Math. und Phys., 19, No. 6 (1968).
4. F. M. Leslie, "Some constitutive equations for anisotropic fluids," Quart. J. Mech. and Appl. Math., 19, No. 3 (1966).
5. G. L. Hand, "A theory of anisotropic fluids," J. Fluid Mech., 13, Part 1 (1964).
6. J. L. Ericksen, "Anisotropic fluid," Arch. Ration. Mech. and Analys., 4, No. 3 (1960).
7. Yu. I. Shmakov and E. Yu. Taran, "A structural-continuum approach to the rheology of polymeric materials," Inzh.-Fiz. Zh., 18, No. 6 (1970).
8. G. B. Jeffery, "The motion of ellipsoidal particles immersed in a viscous fluid," Proc. Roy. Soc., Ser. A, 102, No. 715 (1922).
9. G. L. Hand, "A theory of dilute suspensions," Arch. Ration. Mech. and Analys., 7, No. 1 (1961).
10. A. Peterlin, "Uber die Viskositat von verdunnten Losungen und Suspensionen in Abhangigkeit von der Teilchenform," Z. Phys., 111, Nos. 3/4 (1938).
11. J. L. Ericksen, "Transversely isotropic fluids," Kolloid. Z., 173, No. 2 (1960).
12. J. L. Ericksen, "Some magnetohydrodynamic effects in liquid crystals," Arch. Ration. Mech. and Analys., 23, No. 4 (1966).