EFFECT OF INTERNAL VISCOSITY AND ELASTICITY OF ELLIPSOIDAL MACROMOLECULES ON THE RHEOLOGICAL BEHAVIOR OF DILUTE POLYMER SOLUTIONS. RHEOLOGICAL EQUATIONS OF STATE

Yu. V. Pridatchenko and Yu. I. Shmakov

UDC 532.529

The structural-continuum approach is used to obtain the rheological equations of state for dilute polymer solutions whose macromolecules can be modeled by an ellipsoid of rotation with internal viscosity and elasticity.

In order to obtain the rheological equations of state for dilute polymer solutions using the structural and structural-continuum approach, a model has to be chosen for the polymer macromolecule. We shall take as a model for the macromolecule an ellipsoidal particle which is impenetrable to the liquid and has internal elasticity and viscosity, assuming at the same time that the particle changes its dimensions when interacting with the dispersive medium, but that it remains an ellipsoid of rotation with the same volume.

In order to obtain the rheological equations of state for the medium under consideration by the structural-continuum approach [1-3] we can use a model of a structural continuum containing a single internal parameter, the vector n_i. The position of the vector in space characterizes the effect the particle orientation, and a change in its modulus gives the effect of particle deformations on the rheological behavior of the solution.

The equations defining a structural continuum of this type have the form [4, 5]

$$t_{ij} = (c_0 + c_1 d_{km} n_k n_m + c_2 N_k n_k)\delta_{ij} + c_3 n_i n_j + c_4 d_{km} n_k n_m n_i n_j + c_5 N_k n_k n_i n_j + c_6 d_{ij} + c_7 d_{ik} n_k n_j + c_8 d_{jk} n_k n_i + c_9 n_i N_j + c_{10} n_j N_i; \tag{1}$$

$$\dot{n}_i = \omega_{ij} n_j + \lambda_1 n_i + \lambda_2 d_{km} n_k n_m n_i + \lambda_3 d_{ij} n_j + \lambda_4 \varepsilon_{ijk} M_j n_k + \lambda_5 f_j n_j n_i, \tag{2}$$

where t_{ij} is the stress tensor, d_{ij} is the deformation rate tensor, $N_i = \dot{n}_i - \omega_{ij} n_j$; ω_{ij} is the vorticity tensor; f_j, M_j are the strength and moment of the forces acting on an element of the microstructure, excluding hydrodynamic forces; c_i and λ_i are rheological functions depending on $n^2 = n_i n_i$; and δ_{ij} and ε_{ijk} are the symmetric and antisymmetric Kronecker symbols.

We associate the direction of the vector n_i with the direction of the axis of rotation of the ellipsoidal particle, and its modulus with the length of the semiaxis of rotation a, setting $n = a$.

To find the rheological functions of the model given by Eqs. (1), (2) we shall look for velocity and pressure perturbations in the Stokes approximation, introduced by the suspended particle into the flow of a dispersive medium, which we will take to be a viscous Newtonian liquid. For boundary conditions we shall impose the requirements that the dispersive medium adhere to the surface of the particle, assuming that the particle deformations are homogeneous, and that the velocity and pressure perturbations should vanish at large distances from the particle. We shall construct a solution to the hydrodynamic problem under consideration by a method used by Jeffery [6] in solving the problem of the behavior of a rigid ellipsoidal particle in a viscous liquid flow. Having obtained a solution in a moving coordinate system x_i attached to the particle (the coordinate origin is at the center of the particle and the axes coincide with the directions of the principal axes on the ellipsoidal particle), we transfer the boundary conditions, specified for the velocity at infinity, to the surface of a sphere of radius R, considerably larger than the possible dimensions of the particle. Finally, we

Kiev. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 3, pp. 94-98, May-June, 1976. Original article submitted April 8, 1975.

obtain the following expressions for the velocity and pressure, valid in the neighborhood of the surface of the sphere under consideration:

$$u_i = u_{0i} + (4/3)[(R^3 - r^3)/R^3 r^3](c_{ki} - c_{ik})x_k - 4x_i[(R^5 - r^5)/R^5 r^5]\Phi + 5[(R^2 - r^2)/R^5]\partial\Phi/\partial x_i;$$
$$p = p_0 - (8\mu/r^5)\Phi - (42\mu/R^5)\Phi,$$

where u_i is the velocity, u_{0i} is the velocity of the unperturbed flow, p is the pressure, p_0 is the pressure in the unperturbed flow, r is the modulus of the radius-vector, μ is the dynamic viscosity coefficient of the solvent, and $\Phi = c_{ij}x_i x_j$;

$$c_{11} = \frac{d_{11}}{6\beta_0''} - \frac{\dot{a}}{6a\beta_0''}; \quad c_{22} = \frac{d_{22}}{4b^2\alpha_0'} + \frac{d_{11}(\beta_0'' - \alpha_0'')}{12b^2\beta_0''\alpha_0'} + \frac{\dot{a}}{12a\beta_0''};$$
$$c_{33} = \frac{d_{33}}{4b^2\alpha_0'} + \frac{d_{11}(\beta_0'' - \alpha_0'')}{12b^2\beta_0''\alpha_0'} + \frac{\dot{a}}{12a\beta_0''}; \quad c_{12} = \frac{\alpha_0 d_{12} + b^2\beta_0'(\omega_{12} + \omega_3)}{2\beta_0'(a^2\alpha_0 + b^2\beta_0)};$$
$$c_{21} = \frac{\beta_0 d_{21} + a^2\beta_0'(\omega_{21} - \omega_3)}{2\beta_0'(a^2\alpha_0 + b^2\beta_0)}; \quad c_{13} = \frac{\alpha_0 d_{13} + b^2\beta_0'(\omega_{13} - \omega_2)}{2\beta_0'(a^2\alpha_0 + b^2\beta_0)}; \tag{3}$$
$$c_{31} = \frac{\beta_0 d_{31} + a^2\beta_0'(\omega_{31} + \omega_2)}{2\beta_0'(a^2\alpha_0 + b^2\beta_0)}; \quad c_{23} = \frac{\beta_0 d_{23} + b^2\alpha_0'(\omega_{23} + \omega_1)}{4b^2\alpha_0'\beta_0};$$
$$c_{32} = \frac{\beta_0 d_{32} + b^2\alpha_0'(\omega_{32} - \omega_1)}{4b^2\alpha_0'\beta_0},$$

where α_0, β_0, α'_0, β_0', α''_0, β''_0 are functions of a, b, defined in [6], b is the equatorial radius of the particle, ω_i is the angular velocity of the particle, and $\dot{a}$ is the rate of change of the semiaxis a.

For the stress tensor σ_{ij} describing the stress state in the polymer solution we shall follow Landau [7], and take the value, averaged over the volume of the sphere under consideration, of the tensor for the stresses which arise in the flow of the dispersive medium perturbed by the suspended particle. The integration is carried out not over the volume, but over the surface of the sphere which has been introduced [7-9]:

$$\sigma_{ij} = -p_0\delta_{ij} + 2\mu d_{ij} + (8\mu V/ab^2)c_{ij}, \tag{4}$$

where V is the volume concentration of suspended particles.

We shall consider the orientation and deformation of a suspended particle. Neglecting the inertial properties of the particle, we have for the equations of orientation

$$M_1^0 + M_1 = 0, \quad M_2^0 + M_2 = 0, \quad M_3^0 + M_3 = 0, \tag{5}$$

where M_i are components of the moment of external forces acting on the particle, M_i^0 are components of the moment of the hydrodynamic forces determined by the solution of the hydrodynamic problem

$$M_1^0 = (32/3)\pi\mu(c_{32} - c_{23}), \quad M_2^0 = (32/3)\pi\mu(c_{13} - c_{31}),$$
$$M_3^0 = (32/3)\pi\mu(c_{21} - c_{12}). \tag{6}$$

Assuming that the properties of the particle are symmetric relative to the axis of rotation ($M_1 = 0$), we obtain from Eqs. (5), (6)

$$c_{23} = d_{23}/4b^2\alpha_0', \quad c_{32} = d_{32}/4b^2\alpha_0'. \tag{7}$$

It then follows from Eqs. (3), (5)-(7) that the orientation of the axis of rotation of the particle is described by the following equations:

$$[(a^2 - b^2)/(a^2 + b^2)]d_{31} + \omega_{31} + \omega_2 - [3(a^2\alpha_0 + b^2\beta_0)/16\pi\mu(a^2 + b^2)]M_2 = 0;$$
$$-[(a^2 - b^2)/(a^2 + b^2)]d_{12} + \omega_{12} + \omega_3 - [3(a^2\alpha_0 + b^2\beta_0)/16\pi\mu(a^2 + b^2)]M_3 = 0. \tag{8}$$

If the particle has the properties outlined above, and if its rheological behavior can be modeled by linear elasticity and viscosity, then using the principle of virtual displacements we obtain the following equation describing the deformation of the particle:

$$\frac{\dot{a}}{a} = -\frac{2ab^2\beta_0' Ga/a_0(1 - q_0/q)}{\mu(2 + 3ab^2\beta_0''\eta/\mu)} + \frac{2d_{11}}{2 + 3ab^2\beta_0''\eta/\mu} + \frac{3a\beta_0'' f}{4\pi\mu(2 + 3ab^2\beta_0''\eta/\mu)}, \tag{9}$$

where G is the shear modulus of the particle material; η is the dynamic viscosity coefficient of the particle material; $q = a/b$; $q_0 = a/b_0$; a_0, b_0 are the value of the semiaxis of rotation and the equatorial radius of the particle in its undeformed state; and f is the external force deforming the particle, excluding hydrodynamic forces.

Considering relations (1), (2) in the moving system of coordinates x_i ($n_1 = a$, $n_2 = n_3 = 0$, $\dot{n}_1 = 1$, $\dot{n}_2 = a\omega_3$, $\dot{n}_3 = -a\omega_2$) and comparing Eq. (1) with Eqs. (4), (3), (7) and Eq. (2) with Eqs. (8), (9), we find the rheological functions appearing in Eqs. (1), (2):

$$
\begin{gathered}
a_0 = -p_0; \quad a_1 = \frac{2\mu\Gamma(\beta_0'' - \alpha_0'')}{3a^3b^4\beta_0''\alpha_0'};\\
c_2 = \frac{2\mu\Gamma}{3a^3b^2\beta_0''}; \quad c_3 = 0;\\
c_4 = \frac{2\mu\Gamma}{a^3b^2}\left[\frac{\alpha_0'' + \beta_0''}{b^2\alpha_0'\beta_0''} - \frac{2(\alpha_0 + \beta_0)}{\beta_0'(a^2\alpha_0 + b^2\beta_0)}\right];\\
c_5 = \frac{2\mu\Gamma}{a^3b^2}\left[\frac{2(a^2 - b^2)}{a^2\alpha_0 + b^2\beta_0} - \frac{1}{\beta_0''}\right]; \quad c_6 = 2\mu\left(1 + \frac{\Gamma}{ab^4\alpha_0'}\right);\\
c_7 = \frac{4\mu\Gamma}{a^3b^2}\left[\frac{\beta_0}{\beta_0'(a^2\alpha_0 + b^2\beta_0)} - \frac{1}{2b^2\alpha_0'}\right];\\
c_8 = \frac{4\mu\Gamma}{a^3b^2}\left[\frac{\alpha_0}{\beta_0'(a^2\alpha_0 + b^2\beta_0)} - \frac{1}{2b^2\alpha_0'}\right];\\
c_9 = \frac{4b^2\mu\Gamma}{a^3b^2(a^2\alpha_0 + b^2\beta_0)}; \quad c_{10} = -\frac{4a^2\mu\Gamma}{a^3b^2(a^2\alpha_0 + b^2\beta_0)};\\
\lambda_1 = -\frac{2ab^2\beta_0''Ga/a_0(1 - q_0/q)}{\mu(2 + 3ab^2\beta_0''\eta/\mu)}; \quad \lambda_2 = \left(\frac{2}{2 + 3ab^2\beta_0''\eta/\mu} - \frac{a^2 - b^2}{a^2 + b^2}\right)\frac{1}{a^2};\\
\lambda_3 = \frac{a^2 - b^2}{a^2 + b^2}; \quad \lambda_4 = \frac{3(a^2\alpha_0 + b^2\beta_0)}{16\pi\mu(a^2 + b^2)}; \quad \lambda_5 = \frac{3\beta_0''}{4\pi\mu(2 + 3ab^2\beta_0''\eta/\mu)}.
\end{gathered}
\tag{10}
$$

Since the vector n_i characterizes the behavior of the microstructure, the average must be taken in Eq. (1) when constructing the rheological equations of state, by using the distribution function F for the angular positions of the axis of symmetry of the particle and its relative dimensions:

$$
\begin{gathered}
T_{ij} = \langle t_{ij}\rangle = (c_0 + \langle c_1 n_k n_m\rangle d_{km} + \langle c_2 N_k n_k\rangle)\delta_{ij} + \\
+ \langle c_4 n_k n_m n_i n_j\rangle d_{km} + \langle c_5 N_k n_k n_i n_j\rangle + \langle c_6\rangle d_{ij} + \\
+ \langle c_7 n_k n_j\rangle d_{ik} + \langle c_8 n_k n_i\rangle d_{jk} + \langle c_9 n_i N_j\rangle + \langle c_{10} n_j N_i\rangle.
\end{gathered}
\tag{11}
$$

The distribution function F satisfies the equation

$$\partial F/\partial t + \partial(F\dot{n}_i)/\partial n_i = 0,$$

where t is the time, and $\dot{n}_i$ is defined by Eqs. (2), (10).

If the external forces acting on an element of the microstructure are a result of Brownian motion only, then M_j and f_j, appearing in Eq. (2), have the form [10, 1]

$$
\begin{gathered}
M_j = -kT\varepsilon_{jkm}(n_k/F)\partial F/\partial n_m;\\
f_j = -kT(1/F)\partial F/\partial n_j,
\end{gathered}
\tag{12}
$$

where k is Boltzmann's constant, and T is the absolute temperature. Using Eqs. (12), (2) we write the rheological equation of state (11) in the form

$$T_{ij} = -p\delta_{ij} + 2\langle\mu_0\rangle d_{ij} + \langle\mu_1 n_i n_j\rangle + \langle\mu_2 n_k n_m n_i n_j\rangle d_{km} + 2\langle\mu_3(d_{ik}n_k n_j + d_{jk}n_k n_i)\rangle, \tag{13}$$

where

$$
\begin{gathered}
p = p_0 - \langle c_2\lambda_1 n^2\rangle - kT\langle 3c_2\lambda_5 n^2 + n(d/dn)(c_2\lambda_5 n^2) + \\
+ (c_9 + c_{10})\lambda_4 n^2\rangle + \langle(c_1 + c_2\lambda_2 n^2 + c_2\lambda_3)n_k n_m\rangle d_{km};\\
\mu_0 = (1/2)c_6, \quad \mu_1 = c_5\lambda_1 n^2 + \lambda_1(c_9 + c_{10}) + kT\{5c_5\lambda_5 n^2 + \\
+ (5\lambda_5 - 3\lambda_4)(c_9 + c_{10}) + n(d/dn)[\lambda_5(c_5 n^2 + c_9 + c_{10})]\};\\
\mu_2 = c_4 + c_5(\lambda_2 n^2 + \lambda_3) + \lambda_2(c_9 + c_{10}); \quad \mu_3 = (1/4)[c_7 + c_8 + \lambda_3(c_9 + c_{10})].
\end{gathered}
$$

In this case the distribution function F satisfies the equation

$$
\begin{gathered}
\partial F/\partial t + kT(\lambda_4 - \lambda_5)n_i n_j \partial^2 F/\partial n_i \partial n_j - kT\lambda_4 n^2 \partial^2 F/\partial n_i \partial n_i + \\
+ \lambda_2 n_i(\partial F/\partial n_i)d_{km}n_k n_m + [\lambda_1 + kT(2\lambda_4 - 4\lambda_5 - nd\lambda_5/dn)]n_i \partial F/\partial n_i + \\
+ (\omega_{ij} + \lambda_3 d_{ij})n_j \partial F/\partial n_i + (3\lambda_1 + nd\lambda_1/dn)F + (5\lambda_2 + nd\lambda_2/dn + (1/n)d\lambda_3/dn)Fd_{km}n_k n_m = 0. \qquad (14)
\end{gathered}
$$

The Brownian motion of the suspended particles and their internal properties appear in Eq. (13) by way of their "direct contribution," obtained on substituting Eqs. (2), (10), (12) in Eq. (11), and through the distribution function F, Eq. (14), which depends on these factors.

We note that the rheological equations of state (13), in which only those forces have been taken into account which arise from the Brownian motion of the particles, coincide in form with the equations of state of a dilute suspension of rigid ellipsoidal particles [3]. A change in internal properties of the suspended particles means that the equations of state, instead of containing rheological constants, contain rheological functions, and the averaging process in these equations is carried out not only over all possible angular positions of the suspended particle, but also over its possible relative dimensions.

LITERATURE CITED

1. Yu. I. Shmakov, P. B. Begoulev, and Yu. V. Pridatchenko, "Structural continuum approach in the rheology of disperse and polymer systems," in: Heat and Mass Transfer [in Russian], Vol. 3, Minsk (1972).
2. Yu. I. Shmakov (Y. I. Schmakov) and P. B. Begoulev, "Structure-continual approach in rheology of disperse and polymer system," Rheol. Acta, 13, No. 3 (1974).
3. Yu. I. Shmakov and E. Yu. Taran, "Structural-continuum approach in the rheology of polymer materials," Inzh.-Fiz. Zh., 18, No. 6 (1970).
4. J. L. Ericksen, "Theory of anisotropic fluids," Trans. Soc. Rheol., 4, 29 (1960).
5. J. L. Ericksen, "Orientation induced by flow," Trans. Soc. Rheol., 6, 275 (1962).
6. G. B. Jeffery, "The motion of ellipsoidal particles immersed in a viscous fluid," Proc. Roy. Soc., A 102, 715 (1922).
7. L. D. Landau and E. M. Lifshits, The Mechanics of Continuous Media [in Russian], Gostekhizdat, Moscow (1954).
8. G. L. Hand, "A theory of dilute suspensions" Arch. Ration. Mech. Anal., 7, 1 (1961).
9. Yu. V. Pridatchenko and Yu. I. Shmakov, "Rheological equations of state for weak polymer solutions with rigid ellipsoidal macromolecules," Zh. Prikl. Mekh. Tekh. Fiz., No. 2 (1972).
10. V. N. Pokorvskii, "Stress, viscosity, and optical anisotropy of a moving suspension of rigid ellipsoids," Usp. Fiz. Nauk, 103, No. 4 (1971).