# RHEOLOGICAL EQUATIONS OF STATE FOR WEAK SOLUTIONS OF POLYMERS WITH RIGID ELLIPSOIDAL MACROMOLECULES

P. B. Begoulev and Yu. I. Shmakov

UDC 532.135:541.182.6

Based on the structural-continuum model, the rheological equations of state are derived for weak solutions of polymers with rigid macromolecules in the shape of triaxial ellipsoids.

The rheological equations of state have been derived in [1, 2], from different viewpoints, for weak solutions of polymers with a rigid ellipsoid of revolution serving as the hypothetical model of the macromolecules. From the structural-continuum viewpoint [1], we will now consider the case where the hydrodynamic model of the polymer macromolecules in solution is a rigid triaxial ellipsoid.

We will use the structural-continuum model [3] for describing the rheological behavior of such a medium. A feature of structural-continuum models is the revised concept of the continuum point, with every point here characterizable not only by the density but also by the rate of change of several inner parameters. We will consider the flow of a structural continuum relative to a stationary Cartesian system of coordinates $\overset{i}{x}$ (i = 1, 2, 3). Assuming that the stress tensor $t_{ij}$ depends on the shear-rate tensor $d_{ij}$ and on two inner parameters, namely the inertia tensor $I_{ij}$ and the angular-velocity tensor $\Omega_{ij}$, we obtain, when $t_{ij}$ is a linear function of $d_{ij}$ and $V_{ij} = \omega_{ij} - \Omega_{ij}$, the following expression for the symmetric part $t_{(ij)}$ and for the asymmetric part $t_{[ij]}$ of the stress tensor:

$$t_{(ij)} = -p\delta_{ij} + \alpha_1 I_{ij} + \alpha_2 d_{ij} + \alpha_3 I_{ij}^2 + \alpha_4 (I_{ik}d_{kj} + d_{ik}I_{kj})$$
$$+ \alpha_5 (I_{ik}V_{kj} - V_{ik}I_{kj}) + \alpha_6 (d_{ik}I_{kj}^2 + I_{ik}^2 d_{kj}) + \alpha_7 (V_{ik}I_{kj}^2 - I_{ik}^2 V_{kj}) + \alpha_8 (I_{ik}V_{km}I_{mj}^2 - I_{ik}^2 V_{km}I_{mj}), \tag{1}$$

$$t_{[ij]} = \beta_1 V_{ij} + \beta_2 (I_{ik}d_{kj} - d_{ik}I_{kj}) + \beta_3 (V_{ik}I_{kj} + I_{ik}V_{kj})$$
$$+ \beta_4 (V_{ik}I_{kj}^2 + I_{ik}^2 V_{kj}) + \beta_5 (d_{ik}I_{kj}^2 - I_{ik}^2 d_{kj}) + \beta_6 (I_{ik}d_{km}I_{mj}^2 - I_{ik}^2 d_{km}I_{mj}), \tag{2}$$

where $\alpha_i$ (i = 1, 2, . . . , 8) and $\beta_k$ (k = 1, 2, . . . , 6) are polynomial functions of the first tensor invariants $I_{ij}$, $I_{ij}^2$, $I_{ik}^3$, $I_{ik}d_{kj}$, $d_{ik}I_{kj}^2$ which do not violate the linearity of the $t_{ij}$ dependence on $d_{ij}$ and $V_{ij}$. Inasmuch as the structural-continuum model (1), (2) is used in setting up the rheological equations of state for solutions of polymers with rigid ellipsoidal macromolecules, we relate the inner parameters $I_{ij}$ and $\Omega_{ij}$ in (1) and (2) to the respective characteristics of ellipsoidal macromolecules.

Let $\overset{1}{\vec{n}}, \overset{2}{\vec{n}}, \overset{3}{\vec{n}}$ be mutually orthogonal unit vectors defining the orientation of an ellipsoidal macromolecule along axes $a$, b, c, respectively, then $I_{ij}$ can be represented as

$$I_{ij} = I_1 \overset{1}{n}_i \overset{1}{n}_j + I_2 \overset{2}{n}_i \overset{2}{n}_j + I_3 \overset{3}{n}_i \overset{3}{n}_j. \tag{3}$$

We will disregard the inner moment of momentum, which makes $t_{[ij]} = 0$ [4], and then, with the aid of (2) and (3), we obtain for the angular-velocity tensor $\Omega_{ij}$

$$\Omega_{ij} = \alpha_{mk} d_{st} \overset{m}{n}_s \overset{k}{n}_t \overset{m}{n}_i \overset{k}{n}_j - \omega_{ij}, \tag{4}$$

T. G. Shevchenko State University, Kiev. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 23, No. 2, pp. 340-344, August, 1972. Original article submitted November 28, 1971.

where $\alpha_{mk} = -\alpha_{km}$ are functions of $\beta_k$ (k = 1, 2, . . . , 6) and $I_1$, $I_2$, $I_3$. Inserting (3) and (4) into (1), with the mutual orthogonality of unit vectors $\overset{i}{\vec{n}}$ taken into consideration, we represent the stress tensor as

$$t_{ij} = -p\delta_{ij} + 2\mu_1 d_{ij} + \mu_2 d_{km} \overset{1}{n}_k \overset{1}{n}_m \overset{1}{n}_i \overset{1}{n}_j + \mu_3 d_{km} \overset{2}{n}_k \overset{2}{n}_m \overset{2}{n}_i \overset{2}{n}_j + \mu_4 d_{km} \overset{2}{n}_k \overset{2}{n}_m \overset{1}{n}_i \overset{1}{n}_j + \mu_5 \overset{1}{n}_i \overset{1}{n}_j + \mu_6 \overset{2}{n}_i \overset{2}{n}_j + \gamma_{km} d_{st} \overset{k}{n}_s \overset{m}{n}_t \overset{k}{n}_i \overset{m}{n}_j, \tag{5}$$

where $\nu_{km} = \nu_{mk}$ (k, m = 1, 2, 3, k ≠ m).

In order to determine the rheological constants in (5), we make use of the stress tensor $\sigma_{ij}$, which applies to our medium in a moving system of coordinates $\overset{i}{\vec{n}}$ and which is related to the ellipsoid as follows [5]:

$$\sigma_{ij} = -p\delta_{ij} + 2\mu d_{ij} + \frac{8\mu\Phi}{abc} A_{ij}, \tag{6}$$

where

$$A_{ij} = \begin{vmatrix} \dfrac{2\alpha_0'' d_{11} - \beta_0'' d_{22} - \nu_0'' d_{33}}{6F}, & \dfrac{d_{12}}{2\nu_0'(a^2+b^2)}, & \dfrac{d_{13}}{2\beta_0'(c^2+a^2)} \\ \dfrac{d_{12}}{2\nu_0'(a^2+\beta^2)}, & \dfrac{2\beta_0'' d_{22} - \nu_0'' d_{33} - \alpha_0'' d_{11}}{6F}, & \dfrac{d_{23}}{2\alpha_0'(b^2+c^2)} \\ \dfrac{d_{13}}{2\beta_0'(c^2+a^2)}, & \dfrac{d_{23}}{2\alpha_0'(b^2+c^3)}, & \dfrac{2\nu_0'' d_{33} - \alpha_0'' d_{11} - \beta_0'' d_{22}}{6F} \end{vmatrix},$$

$F = (\alpha_0''\beta_0'' + \alpha_0''\nu_0'' + \beta_0''\nu_0'')$, $\alpha_0$, $\beta_0$, $\nu_0$, $\alpha_0'$, $\beta_0'$, $\nu_0'$, $\alpha_0''$, $\beta_0''$, $\nu_0''$ are functions of $a$, b, c [6]. Transformation of Eq. (5) to the moving system of coordinates $\overset{1}{\vec{n}}$ (1, 0, 0), $\overset{2}{\vec{n}}$ (0, 1, 0), $\overset{3}{\vec{n}}$ (0, 0, 1) and comparison with (6) will yield the following expressions for the rheological constants:

$$\mu_1 = \mu\left(1 + \frac{2\Phi}{abc} \cdot \frac{\nu_0''}{F}\right), \tag{7}$$

$$\mu_2 = \frac{4\mu\Phi}{abc} \cdot \frac{\alpha_0'' - \gamma_0''}{F}, \tag{8}$$

$$\mu_3 = \frac{4\mu\Phi}{abc} \cdot \frac{\beta_0'' - \nu_0''}{F}, \tag{9}$$

$$\mu_4 = 0, \tag{10}$$

$$\nu_{12} = \frac{4\mu\Phi}{abc}\left(\frac{1}{\nu_0'(a^2+b^2)} - \frac{\nu_0''}{F}\right), \tag{11}$$

$$\nu_{13} = \frac{4\mu\Phi}{abc}\left(\frac{1}{\beta_0'(a^2+c^2)} - \frac{\nu_0''}{F}\right), \tag{12}$$

$$\nu_{23} = \frac{4\mu\Phi}{abc}\left(\frac{1}{\alpha_0'(b^2+c^2)} - \frac{\nu_0''}{F}\right). \tag{13}$$

Based on a comparison of (5) and (6), we ought to let $\mu_5 = \mu_6 = 0$, but the terms $\mu_5 \overset{1}{n}_i \overset{1}{n}_j$, $\mu_6 \overset{2}{n}_i \overset{2}{n}_j$, as well as $\mu_1 n_i n_j$ in the case of an ellipsoid of revolution in [1] may represent stresses due to rotational Brownian movement not accounted for in [5]. Leaving $\mu_5$ and $\mu_6$ undetermined as yet, we will consider the expression (5) averaged through the distribution function in [7], which characterizes the orientation of an ellipsoidal macromolecule due to hydrodynamic forces and rotational Brownian movement,

$$\langle t_{ij} \rangle = -p\delta_{ij} + 2\mu_1 d_{ij} + \mu_2 d_{km} \langle \overset{1}{n}_k \overset{1}{n}_m \overset{1}{n}_i \overset{1}{n}_j \rangle$$
$$+ \mu_3 d_{km} \langle \overset{2}{n}_k \overset{2}{n}_m \overset{2}{n}_i \overset{2}{n}_j \rangle + \mu_5 \langle \overset{1}{n}_i \overset{1}{n}_j \rangle + \mu_6 \langle \overset{2}{n}_i \overset{2}{n}_j \rangle + \nu_{km} d_{st} \langle \overset{k}{n}_s \overset{m}{n}_t \overset{k}{n}_i \overset{m}{n}_j \rangle, \tag{14}$$

is the rheological equation of state for our medium, where $\mu_1$, $\mu_2$, $\mu_3$, and $\nu_{km}$ are defined by Eqs. (7)-(13), respectively.

In order to determine the rheological constants $\mu_5$ and $\mu_6$, we will find the dissipation of mechanical energy S in a simple shear flow:

$$v_i = G_{ij}\overset{j}{x},\ G_{ij} = \begin{vmatrix} 0 & 0 & 0 \\ K & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix}, \tag{15}$$

due to the occurrence of rotational Brownian movement.

According to [8], this component of mechanical energy dissipation is

$$S = \frac{4\mu\Phi K}{abc} \Big\langle \Big[ \frac{(c^2-b^2)h_{32} - (c^2+b^2)o_{32}}{b^2\beta_0 + c^2\nu_0} W_1 + \frac{(b^2-a^2)h_{21} - (b^2+a^2)o_{21}}{a^2\alpha_0 + b^2\beta_0} W_3 + \frac{(a^2-c^2)h_{13} - (a^2+c^2)o_{13}}{a^2\alpha_0 + c^2\nu_0} W_2 \Big] \Big\rangle, \tag{16}$$

where

$$\|h_{ij}\| = \frac{1}{2}(A^{-1}GA) + \frac{1}{2}(A^{-1}GA)',$$

$$\|o_{ij}\| = \frac{1}{2}(A^{-1}GA) - \frac{1}{2}(A^{-1}GA)',$$

Here A is the transformation matrix from the moving system of coordinates $\overset{i}{\vec{n}}$ to the stationary system of coordinates $\overset{i}{x}$, the prime sign denoting a transformation. After performing several operations, we can write relation (16) as

$$S = \frac{\mu\Phi K}{abc}\Big[\frac{D_r^2(a^2-c^2)}{c^2\nu_0 + a^2\alpha_0}(8\langle \overset{1}{n}_1\overset{1}{n}_2\rangle + 4\langle \overset{2}{n}_1\overset{2}{n}_2\rangle) + \frac{D_r^3(a^2-b^2)}{a^2\alpha_0 + b^2\beta_0}(4\langle \overset{1}{n}_1\overset{1}{n}_2\rangle - 4\langle \overset{2}{n}_1\overset{2}{n}_2\rangle) + \frac{D_r^1(b^2-c^2)}{b^2\beta_0 + c^2\nu_0}(8\langle \overset{2}{n}_1\overset{2}{n}_2\rangle + 4\langle \overset{1}{n}_1\overset{1}{n}_2\rangle)\Big]. \tag{17}$$

It follows from (17) that the terms $\mu_5\langle \overset{1}{n}_i\overset{1}{n}_j\rangle$, $\mu_6\langle \overset{2}{n}_i\overset{2}{n}_j\rangle$ in (14) are indeed stresses due to rotational Brownian movement and that $\mu_5$, $\mu_6$ are, respectively:

$$\mu_5 = \frac{\mu\Phi}{abc}\Big[8\frac{D_r^2(a^2-c^2)}{a^2\alpha_0 + c^2\nu_0} + 4\frac{D_r^3(a^2-b^2)}{a^2\alpha_0 + b^2\beta_0} + 4\frac{D_r^1(b^2-c^2)}{b^2\beta_0 + c^2\nu_0}\Big], \tag{18}$$

$$\mu_6 = \frac{\mu\Phi}{abc}\Big[4\frac{D_r^2(a^2-c^2)}{a^2\alpha_0 + c^2\nu_0} + 4\frac{D_r^3(b^2-a^2)}{a^2\alpha_0 + b^2\beta_0} + 8\frac{D_r^1(b^2-c^2)}{b^2\beta_0 + c^2\nu_0}\Big]. \tag{19}$$

In the special case where b = c, the rheological equations of state (14) become the earlier derived equations of state [1] for weak solutions of polymer macromolecules with a rigid ellipsoid of revolution as the hypothetical hydrodynamic model. When $a$ = b = c, Eqs. (14) yield Einstein's classical result [9].

## NOTATION

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| $t_{ij}$ | is the stress tensor; |
| p | is the isotropic pressure; |
| $\delta_{ij}$ | is the Kronecker delta; |
| $d_{ij}$ | is the strain-state tensor; |
| $\omega_{ij}$ | is the velocity-vortex tensor; |
| $\Omega_{ij}$ | is the inner parameter: angular-velocity tensor; |
| $I_{ij}$ | is the inner parameter: inertia tensor; |
| $\overset{i}{x}$ | is the stationary Cartesian system of coordinates; |
| $a$, b, c | are the semiaxes of an ellipsoid; |
| $\overset{i}{\vec{n}}$ | are the unit vectors oriented along the ellipsoid semiaxes $a$, b, c, respectively; |

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| $\mu_i$, $\nu_{km}$ | are the rheological constants; |
| $\mu$ | is the dynamic viscosity of the solvent; |
| $\Phi$ | is the volume concentration of macromolecules in the solution; |
| $D_r^i$ | is the rotational diffusivities of the ellipsoid; |
| $\langle\ \rangle$ | is the symbol of averaging; |
| $\alpha_0$, $\beta_0$, $\nu_0$, $\alpha_0'$, $\beta_0'$, $\nu_0'$, $\alpha_0''$, $\beta_0''$, $\nu_0''$ | are the functions of $a$, b, c according to the Jeffery theory; |
| S | is the dissipation of mechanical energy, per unit volume, due to rotational Brownian movement; |
| $v_i$ | are the velocity components in the stationary system of coordinates; |
| $W_i$ | is the angular velocity of ellipsoid, in the moving system of coordinates, due to rotational Brownian movement. |

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