STRUCTURE-CONTINUOUS CONCEPT IN THE RHEOLOGY OF POLYMER SUBSTANCES

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Rheological equations of state are postulated for weak suspensions of rigid ellipsoidal particles on the basis of the structure-continuous concept.

In setting up the rheological equations of state for polymer substances one usually starts out from either of two alternative concepts. The first concept is a phenomenological (macroscopic) one based on the premise that the medium under consideration is continuous. The rheological equations of state are derived here from the general laws of mechanics and phenomenological thermodynamics with certain assumptions concerning the given medium (isotropy, elasticity, etc.). The rheological constants or the rheological functions for this substance which appear in those equations are determined experimentally. Without dwelling on an enumeration of existing phenomenological theories for the rheology of polymers, we will refer here to a rather complete survey of such theories in [1] by Truesdell and Noll.

The other concept – a structural (microscopic) one – defines the rheological behavior of complex substances in terms of known rheological properties of their components, with the macroscopic properties expressed by average microscopic characteristics. This concept has been elaborated successfully, for instance, in developing the theory of rigid balls or ellipsoids in a dilute suspension. Such substances include various colloidal suspensions, certain biopolymer solutions, and also solutions of particles with a supermolecular structure (e.g., particles of various viruses or micellar aggregates of molecules) [2].

It has been suggested in the works by Einstein [3], Jeffery [4], Peterlin [5], Kuhn [6], Saito [7], and Pokrovskii [8, 9] that the solid phase consists of rigid balls [3] or monodispersed ellipsoids [4, 5, 6, 7, 8, 9] while all the remaining space is filled with a Newtonian liquid. It is also suggested that the dimensions of the rigid particles in suspension are much larger than the dimensions of the solvent molecules (but sufficiently small to be subject to a rotational Brownian motion [5, 6, 7, 8, 9]) – thus one may treat the solvent as a continuous medium and apply the equations from the mechanics of continuous media. The applicability of the said theories is limited to dilute suspensions, since interaction between particles of the solid phase is not taken into account.

Where polymer substances are concerned, the structural theories, which are capable of relating all rheological characteristics to the molecular structure of the medium, are natually preferred to the phenomenological theories including information about the molecular structure on an a priori basis. In many cases, however, where the molecular structure of the medium is sufficiently complex to make the development of a structural theory very difficult, a phenomenological concept remains the only feasible one.

A number of models has been proposed during the last 10-15 years which can be classified as structure-continuous ones [10-21]. The first attempts at agglomerating the particles of a continuum into a structure were made by Duhem [22]. His ideas were further developed in the theory of an elastic medium by Cosserat [23], where every particle has six degrees of freedom so that a possible spatial orientation of particles can be accounted for. This theory was put into a final form in [24].

The idea of using a structural continuum for studying the motion of a liquid which contains a flexible or rigid substructure (colloidal solutions, high-polymer solutions) must be credited to Anzelius [25].

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Ericksen has developed this idea into his theory of anisotropic liquids [17, 18]. In order to describe the possible orientations and deformations of substructure particles in the liquid, Ericksen introduces at every point in the liquid an orientation vector **n**. Postulating the dependence of the stress tensor t_{ij} components on the strain rate tensor d_{ij} components and on the direction vector $\mathbf{n} = \{n_i\}$, he derives equations which define a simply anisotropic liquid (with an unstrainable substructure $|\mathbf{n}| = 1$):

$$t_{ij} = -p\delta_{ij} + 2\mu d_{ij} + (\mu_1 + \mu_2 d_{km} n_k n_m) n_i n_j + 2\mu_3 (d_{jk} n_k n_i + d_{ik} n_k n_j), \tag{1}$$

$$\dot{n}_i = \omega_{ij} n_j + \lambda (d_{ij} n_j - d_{km} n_k n_m n_i) \tag{2}$$

on the basis of the invariance principle [26] and of the results obtained by Rivlin [27].

The rheological constants μ, μ_1, μ_2, μ_3, λ are determined by experiment or by juxtaposition with other theories.

In this article Eqs. (1), (2) defining a simple anisotropic liquid will be applied to obtain the rheological equations of state for suspensions of rigid ellipsoidal particles. The rheological constants are determined with the aid of the structural theory by Jeffery [4] if the equivalent radius of the ellipsoidal particles $r = \sqrt[3]{ab^2} > 4 \cdot 10^{-6}$ m*) or with the aid of the Saito theory [7] when $r < 10^{-6}$ m.

It has been shown in [4] that, in the Stokes approximation, the equations of motion for a rigid ellipsoid suspended in an incompressible Newtonian liquid which flows with shear

$$v_x = 0, \quad v_y = Kx, \quad v_z = 0; \quad K = \text{const}, \tag{3}$$

are

$$\begin{aligned} \omega_\varphi &\equiv \dot{\varphi} = \frac{K}{2}(1 + q\cos 2\varphi), \\ \omega_\theta &\equiv \dot{\theta} = \frac{K}{4} q \sin 2\varphi \sin 2\theta. \end{aligned} \tag{4}$$

It has been assumed here that the transport velocity of the ellipsoid is the same as the velocity of the liquid.

It follows from these equations, which have been verified experimentally by Mason [28], that ellipsoidal particles orient themselves kinematically along the direction of flow. The orientation of particles is characterized here by the position distribution function of the major axes $p(\varphi)$ determined from Eq. (5) [29]:

$$\frac{d}{d\varphi}[p(\varphi)\dot{\varphi}] = 0. \tag{5}$$

When the particles have an equivalent radius $r < 10^{-6}$ m [5], it becomes necessary to take into account their rotational Brownian motion, which impedes this orientation. In that case the orientation of a particle is characterized by the distribution function $F(\varphi, \theta)$ which the Fokker–Planck equation of steady state

$$D_r \Delta F = \operatorname{div}(F\vec{\omega}) \tag{6}$$

defines.

When one considers the shearing flow (3) of a simple anisotropic Ericksenian liquid (1), (2) at $|\lambda| \leq 1$, it is easy to ascertain that the equations of orientation (2) are the same as the equations of motion for a rigid ellipsoid suspended in an incompressible Newtonian liquid which flows with shear (3). Indeed, when

$$n_x = \cos\varphi \sin\theta, \quad n_y = \sin\varphi \sin\theta, \quad n_z = \cos\theta,$$

Eqs. (2) for the flow (3) are the same as the Jeffery equations [4]. The orientation vector **n** here coincides directionally with the major axis of the ellipsoid (Fig. 1) while the constant $\lambda = q$. The identicity of the

*Suspensions are classified according to the equivalent radius of ellipsoidal particles when water is the solvent ($\mu_0 = 0.001$ N·sec/m^2) [5].

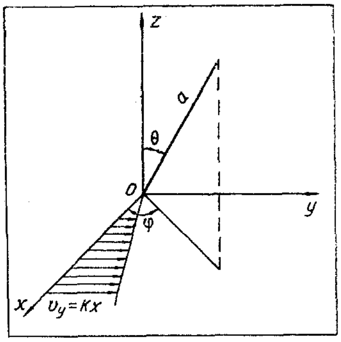

Fig. 1. Stationary system of coordinates for analyzing the motion of a rigid ellipsoid within a shearing flow $v_y = Kx$, $v_x = v_z = 0$ of a Newtonian liquid.

Ericksen equations of orientation and the Jeffery equations, together with the rather general form of relation (1), suggest that one try to use Eq. (1), which defines a simple anisotropic Ericksenian liquid and which is averaged through the respective major axes distribution function (5) or (6) for ellipsoidal particles, as the rheological equation of state for dilute suspensions of rigid ellipsoidal particles

$$T_{ij} = -p\delta_{ij} + 2\mu d_{ij} + \mu_1 \langle n_i n_j \rangle + \mu_2 d_{km} \langle n_k n_m n_i n_j \rangle + 2\mu_3 (d_{jk} \langle n_k n_i \rangle + d_{ik} \langle n_k n_j \rangle). \tag{7}$$

In order to determine the rheological constants which appear in the equation of state (7) for suspensions of particles with an equivalent radius $r > 4 \cdot 10^{-6}$ m, the effective viscosity μ_0 found from Eq. (7) for a simple shearing flow (3)

$$\mu_a = \mu + \frac{\mu_1}{2K} \langle \sin 2\varphi \sin^2\theta \rangle + \frac{\mu_2}{4} \langle \sin^2 2\varphi \sin^4\theta \rangle + \mu_3 \langle \sin^2\theta \rangle, \tag{8}$$

will be compared with the expression for effective viscosity found by Jeffery on the basis of a structural concept [4]. We obtain here the following expressions for the rheological constants:

$$\mu = \mu_0 \left(1 + \frac{\Phi}{ab^4\alpha_0'}\right), \tag{9}$$

$$\mu_1 = 0, \tag{10}$$

$$\mu_2 = 2\mu_0 \frac{\Phi}{ab^2} \left(\frac{\alpha_0''}{b^2\alpha_0'\beta_0''} + \frac{1}{b^2\alpha_0'} - \frac{4}{\beta_0'(a^2+b^2)}\right), \tag{11}$$

$$\mu_3 = \mu_0 \frac{\Phi}{ab^2} \left(\frac{2}{\beta_0'(a^2+b^2)} - \frac{1}{b^2\alpha_0'}\right). \tag{12}$$

These relations agree with those obtained by Hand [30] on a different premise.

In averaging the expression (7) through the distribution function defined by Eq. (5), we obtain for the shearing flow

$$T_{yy} - T_{zz} = 0, \quad T_{xx} - T_{zz} = 0,$$

$$T_{xy} = \left\{\mu + \frac{\mu_2}{2} \frac{p^2}{(p^2-1)^2} \left[\frac{C^2(p^2+1)+2}{\sqrt{(C^2p^2+1)(C^2+1)}} - 2\right] + \mu_3 \left(1 - \frac{1}{\sqrt{(C^2p^2+1)(C^2+1)}}\right)\right\} K, \quad T_{yz} = T_{xz} = 0.$$

The distribution function for the orbit constant C has been found experimentally by Mason [31].

In this way, weak suspensions of rigid ellipsoidal particles with $r > 4 \cdot 10^{-6}$ m behave like Newtonian liquids whose coefficient of the effective viscosity depends on the viscosity of the solvent μ_0, on the volume concentration of particles, on the relative dimensions of particles, and on the distribution function of the orbit constant C.

For suspensions of rigid ellipsoidal particles with $r < 10^{-6}$ m the rheological constants are determined by comparing the effective viscosity from (8) with the expression for effective viscosity based on the structural concept by Saito [7], which in the determination of effective viscosity accounts – unlike the Jeffery concept – for rotational Brownian motion occurring in suspensions of particles with $r < 10^{-6}$ m.

In this case the expressions for μ, μ_2, μ_3 are the same as (9), (11), (12), respectively, while

$$\mu_1 = 12\mu_0 D_r \frac{\Phi}{ab^2} \frac{a^2-b^2}{a^2\alpha_0 + b^2\beta_0}. \tag{10'}$$

By averaging the stress tensor (7) components through the distribution function $F(\varphi, \theta)$ obtained in [5], we obtain from Eq. (6) for a shearing flow

$$T_{xx} - T_{zz} = \mu_1 \frac{\lambda}{5} \frac{\sigma^2}{\sigma^2+36} \left(\frac{3}{7}\lambda - 1\right) + \mu_2 D_r \frac{4\lambda}{7} \frac{\sigma^2}{\sigma^2+36} \left(\frac{3}{5} - \frac{2\lambda}{3} \frac{\sigma^2}{\sigma^2+100}\right) + \mu_3 \frac{12\lambda D_r}{5} \frac{\sigma^2}{\sigma^2+36}, \tag{13}$$

$$T_{yy}-T_{zz}=\mu_1\frac{\lambda}{5}\frac{\sigma^2}{\sigma^2+36}\left(\frac{3}{7}\lambda-1\right)+\mu_2 D_r\frac{4\lambda}{7}\frac{\sigma^2}{\sigma^2+36}\times\left(\frac{3}{5}+\frac{2\lambda}{3}\frac{\sigma^2}{\sigma^2+100}\right)+\mu_3\frac{12\lambda D_r}{5}\frac{\sigma^2}{\sigma^2+36}, \quad (14)$$

$$T_{xy}=\left\{\mu+\mu_1\frac{6}{5}\frac{\lambda}{D_r}\frac{1}{\sigma^2+36}+\mu_2\left[\frac{1}{15}+\frac{\lambda^2\sigma^2}{\sigma^2+36}\times\left(\frac{3}{350}-\frac{1}{42}\frac{\sigma^2-60}{\sigma^2+100}\right)+\mu_3\left(\frac{2}{3}+\frac{2}{35}\frac{\lambda^2\sigma^2}{\sigma^2+36}\right)\right\}K, \quad (15)$$

$$T_{xz}=0,\quad T_{yz}=0. \quad (16)$$

It follows from (13), (14), (15), (16) that the media considered here distinctly display Newtonian properties: the Weissenberg effect [32] and the dependence of effective viscosity on the shearing rate. For the case under consideration here the effective viscosity as a function of σ and p has been tabulated by Sheraga [33] with the averaging done on a computer. Sheraga's results have been confirmed experimentally by Yang [34].

Thus, the Newtonian behavior of rigid ellipsoidal particles in dilute suspensions is related to the rotational Brownian motion and is evident in suspensions of particles with an equivalent radius $r < 10^{-6}$ m.

The derived equations (7) with the rheological constants determined, then, make it possible to analyze various simple flow modes of suspensions containing rigid ellipsoidal particles. Accordingly, the authors have analyzed simple elongation, flow in a shallow channel, a Poissonian flow, and other kinds of flow, using for the averaging in (7) the distribution functions determined by Pokrovskii for any arbitrary flow with small velocity gradients.

The equation of state for media under consideration here and analogous to (7) has been derived by Pokrovskii [8] from the microrheological point of view (structural concept). From a comparison of relation (7) with the stress tensor derived by Pokrovskii, one can draw the following conclusions.

1. In the absence of Brownian motion, the stress tensor (7) is identical to the Pokrovskii stress tensor.

2. Brownian motion is accounted for by Pokrovskii [8] analogously as Kuhn [6] has done it, while the authors of this study have used the Saito theory [7] and, consequently, certain differences between Eq. (7) and the results of the Pokrovskii analysis [8] are in evidence. It is easy to show, nevertheless, that the expressions for shear viscosity derived on the basis of the respective theories agree. This confirms as Saito and Sugita have predicted [35], the equivalency of the final results obtained on the basis of the Saito theory [7] and the Kuhn theory [6].

NOTATION

t_{ij}	is the stress tensor of a simple anisotropic Ericksenian liquid;
p	is the isotropic pressure;
δ_{ij}	is the Kronecker delta;
d_{ij}	is the strain rate tensor;
ω_{ij}	is the velocity vortex tensor;
n_i	is the orientation vector;
μ, μ_1, μ_2, μ_3, λ	are the rheological constants;
r	is the equivalent radius of rigid elliptical particles;
a, b	are the major and minor semiaxes of an ellipsoid;
v_x, v_y, v_z	are the velocity components in Cartesian coordinates x, y, z;
ω_φ, ω_θ	are the components of angular velocity in spherical coordinates r, φ, θ;
$q = (a^2 - b^2)/(a^2 + b^2)$;	
D_r	is the rotational diffusivity;
$\vec{\omega}$	is the angular velocity vector;
n_x, n_y, n_z	are the orientation vector components in Cartesian coordinates x, y, z;
T_{ij}	is the stress tensor of a suspension containing rigid ellipsoidal particles;
$\langle\ \rangle$	is the symbol of averaging through the distribution function;
μ_0	is the dynamic viscosity of the solvent;

Φ is the volume concentration of suspended particles;
$\alpha_0, \alpha_0', \alpha_0'', \beta_0, \beta_0', \beta_0''$ are the functions of a and b defined in the Jeffery theory;
$p = a/b$;
$\sigma = K/D_r$.

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