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PHENOMENOLOGICAL STRUCTURAL MODEL AND SOME RESULTS OF INVESTIGATING THE FLOW OF CONCENTRATED SOLUTIONS OF HIGH POLYMERS

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The mechanical behavior of concentrated solutions of high polymers is investigated on the basis of a previously proposed phenomenological structural model.

1. The most important problem in the investigation of heat and mass transfer in anomalously viscous media (solutions and melts of high polymers, oils, viscoelastic separating agents, etc.) is the closing of the system of equations of motion. On the basis of a fluctuation network model of concentrated solutions of high polymers in a low-molecular solvent (in the form of a collection of effective points of friction joined spatially by elastic subchains with kinetic rigidity) an expression was obtained in [1] for the stress tensor in terms of the moments of the distribution function for the probability density of the position of the friction points and a kinetic equation for these moments:

\[ p_{ij} = -p_{0} \delta_{ij} + 2p \varepsilon_{ij} + \varepsilon_{ij} (x_{i}x_{j} - \delta_{ij}) + \eta (x_{i}x_{k}x_{j} + x_{i}x_{k}x_{j} - 2(x_{i}x_{j} - \delta_{ij})/x \]  \\

\[ d_{ij}(x_{i}x_{j}) = (x_{i}x_{j} - \alpha_{ij}) + (x_{i}x_{k}) (x_{j}x_{k} - \alpha_{ij}) \]  \\

Here, \( p_{0} = p + \tau \sigma / 3 \) is an arbitrary scalar, \( p \) is the hydrostatic pressure, \( \delta_{ij} \) is the Kronecker delta, \( \tau \sigma \) is the trace of the excess stress tensor, \( p \) is the viscosity of the solvent, \( \varepsilon_{ij} \) is the tensor of the velocity gradients, \( \varepsilon_{ij} \) is the symmetric rate-of-strain tensor, \( \varepsilon \) is the modulus of the high elasticity, \( \eta = 0.5 \sigma \varepsilon \) is the internal viscosity of the subchains of the polymer network, \( \alpha \) is the kinetic rigidity of the polymer subchains, \( x \) is the time of internal structural rearrangements (the characteristic relaxation time) after the lifting (or application) of a strain, \( V \) is the volume, and \( t \) is the time.

Correlation analysis of the applicability of the model under different deformation conditions showed [2] that in the range \( \varepsilon_{12} = 0-100 \) sec\(^{-1} \) the model can be used under both steady and transient conditions of deformation.

The basic idea in the derivation of the rheological equation of state was first to describe the physical behavior of the viscoelastic medium at the structural level, and then go over by means of spatial averaging to a macroscopic description of the stressed state of the medium. The derivation of the equation did not foresee a rigorous treatment of the statistical properties of the microscopic models of the polymer systems. A phenomenological structural approach was used, this making it possible at the structural
level with allowance for the fundamental properties (ε, κ, α) to identify an admissible class of viscoelastic media (concentrated solutions of high polymers) described by a nonlinear tensor rheological equation of state with the corresponding parameters determined experimentally.

The following requirements are imposed on the equation of state: 1) it must be physically clear and simple for applications; 2) in conjunction with the conservation laws, it must describe the main experimentally observed features of the mechanical behavior of viscoelastic media (nonlinearly viscous properties, anisotropy of the normal stresses, relaxation phenomena [2]); 3) it must have predictive power and be capable of modification if the results of calculations deviate from the experimental data; 4) the equation must relate the experimentally measured macroscopic characteristics of the flow of the medium to its model microscopic structure.

Already in its original formulation the rheological system of equations (1.1) and (1.2) gives an interesting result. Equation (1.1) determines the stress tensor with allowance for the disequilibrium of the deformation process; Eq. (1.2) characterizes the transient behavior of the characteristics of the stressed state, for example, on transition to the state of thermodynamic equilibrium.

Setting \( ν_{ij} = 0 \) in (1.2), we find \( \langle (x_i x_j) - δ_{ij} \rangle = \exp(-2t/τ) \). It can be seen that the state of thermodynamic equilibrium \( \langle (x_i x_j) - δ_{ij} \rangle = 0 \) is achieved more rapidly, the smaller \( κ \).

For fluids for which \( κ = 0 \), \( (x_i x_j) = δ_{ij} \). For crystalline and amorphous bodies \( κ = ∞ \), and therefore \( (x_i x_j) - δ_{ij} \) becomes unity. The Deborah number \( De = κ / τ \) corresponds to the intermediate region characteristic of viscoelastic media (\( T \) is the time scale during which the fluid is subjected to a variable strain).

With allowance for (1.1) and (1.2), the system of equations of motion for the concentrated solutions of high polymers takes the form

\[
\begin{align*}
\dot{p}_{ij} + w_i \dot{w}_j - w_j \dot{w}_i &= -\partial_i \rho \dot{w} + \gamma_i \partial_t \left( \frac{1}{2} (x_i x_j) - \delta_{ij} \right) ,
\end{align*}
\]

and making the asymptotic representation of \( (x_i x_j) \) with respect to \( \varepsilon_{ij} \) that is usual in hydrodynamics, we can write in the first approximation

\[
\begin{align*}
\dot{p}_{ij} &= -\partial_i \rho \dot{w}_j + 2μ \varepsilon_{ij} - \partial_j \varepsilon_{ij} \frac{δ}{δt} (x_i x_j) - δ_{ij} ,
\end{align*}
\]

Because of this, we obtain from (1.3) the following particular result for a relaxing flow of fluid:

\[
\begin{align*}
\dot{w}_i + w_j \dot{w}_j &= -\partial_i \rho \dot{w} + \gamma_i \partial_t \left( \frac{1}{2} \Delta w_i + w_i / \partial_j \Delta w_j / \partial_t \right) ,
\end{align*}
\]

Here, \( \mu_p = 0.5 κ \) is the rheodynamic viscosity, and \( \langle w \rangle \) is the mean flow velocity. It is clear from what follows that the tensor nonlinearity in Eq. (1.3) is responsible for the anisotropy of the normal stresses, while the terms in the round brackets are responsible for the relaxation phenomena in the unsteady rheological flows.

The expression in the square brackets of Eq. (1.3) can be interpreted as some operation of the type \( \delta / \delta t \) with negative nonlinear terms applied to a second-rank tensor [2] with components \( (x_i x_j) \).

Writing (1.1) in the form

\[
\begin{align*}
p_{ij} &= -p \delta_{ij} + 2μ \varepsilon_{ij} - μ_p \frac{δ}{δt} (x_i x_j) - δ_{ij} ,
\end{align*}
\]

and making the asymptotic representation of \( (x_i x_j) \) with respect to \( \varepsilon_{ij} \) that is usual in hydrodynamics, we can write in the first approximation

\[
\begin{align*}
p_{ij} &= -p \delta_{ij} + 2μ \varepsilon_{ij} - μ_p \varepsilon_{ij} / \partial t ,
\end{align*}
\]

Here, the dimensionless number \( De / Re_p \) measures the deviation of the relaxing flow from the state of local thermodynamic equilibrium. It characterizes the dissipative phenomena in relaxation, which, as can be seen from the model, can be manifested only in nonstationary flows or flows which have not reached a constant velocity. The ratio \( L / L \) can be regarded as the rate of relaxation of the process at the scale \( L \), and (\( ε / p \))^0.5 ~ \( v_\kappa \) as the specific propagation velocity of shear perturbations. In stationary flows that have not yet reached a constant velocity, \( De \approx ε (ω) / L \), where \( L \) is the linear dimension of the region in which the fluid is in a field of changing velocity.