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AN INITIAL APPROXIMATION IN THE THEORY OF MICROVISCOELASTICITY OF LINEAR POLYMERS AND ASSOCIATED NONLINEAR EFFECTS

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In order to model polymer fluid flows within the framework of continuum mechanics, it is necessary to write a rheological state equation that establishes a relationship between the stress tensor for a polymer system and the velocity-gradient tensor. This can be done either by a phenomenological approach [1], generalizing the available experimental data, or by using some model concepts of the structure of polymer materials [2–13]. However, both approaches will probably not provide us with a simple enough rheological constitutive relation suitable for a description of various flows of linear polymer solutions and melts. Therefore, the problem of construction of a succession of rheological constitutive relations taking new and more subtle effects into account at each step is of great importance. The success of such a procedure is determined by the selection of an initial approximation and by the rules of transition to subsequent approximations.

At various times the well-known BKZ [1] or Doi–Edwards [2, 4] rheological models have been proposed as initial approximations.

In the present work, zeroth approximations of the molecular theory of viscoelasticity [5–9] for given small parameters are considered, and the possibility of using these relations as a first approximation in the construction of a sequence of rheological constitutive relations is demonstrated.

Rheological Constitutive Relation. The model concepts coming from the simulation of polymer-chain motion serve as a basis for different microstructural approaches to the description of the dynamics of polymer systems. Here, statement of the equations of dynamics of a macromolecule is not possible without some additional assumptions. Two essential assumptions are used most often: 1) a monomolecular approximation, in which a single selected macromolecule moving in an effective relaxing medium formed by a solvent and by the other macromolecules is considered instead of the entire set of macromolecules in the volume; 2) the ability to consider the motion of a selected macromolecule as the motion of N ($N \gg 1$) centers of friction (beads) linked together one after another by elastic entropy forces (springs). These assumptions, which are only hypothetical, bring us to the equations of dynamics of a macromolecule [5–8]:

$$
\begin{gathered}
m\frac{d}{dt}\psi_i^\alpha = \Gamma_i^\alpha + T_i^\alpha - 2T\mu\lambda_\alpha\rho_i^\alpha + \Phi_i^\alpha, \\
\tau\frac{D}{Dt}\Gamma_i^\alpha + \Gamma_i^\alpha = -\zeta B_{ij}^\alpha(\psi_j^\alpha - \nu_{jl}\rho_l^\alpha), \\
\tau\frac{D}{Dt}T_i^\alpha + T_i^\alpha = -\zeta E_{ij}^\alpha(\psi_j^\alpha - \omega_{jl}\rho_l^\alpha).
\end{gathered}
\tag{1}
$$

Here ρ_i^α and ψ_i^α are the generalized coordinate and velocity; m is the mass of a bead; Γ_i^α is the force of hydrodynamic entrainment; T_i^α is the force of internal viscosity; Φ_i^α is a random force; $2T\mu\lambda_\alpha$ is the coefficient of elasticity, τ is the relaxation time of the environment; ζ is the coefficient of friction of a bead in a monomeric fluid; B_{ij}^α and E_{ij}^α are the tensor coefficients of friction of a bead; ν_{ij} is the velocity-gradient tensor; ω_{ij} is the antisymmetrized velocity-gradient tensor; D/Dt is the Jauman's tensor derivative; the Latin indices i,

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$j, \ldots = 1, 2, 3$ denote the numbers of the spatial Cartesian coordinates, while the Greek indices α, $\beta, \ldots = 1, 2, \ldots, N$ denote the numbers of the generalized coordinates in a macromolecule.

Equations (1) lead us to the following expression for the stress of the polymer system σ_{ik} in terms of the internal thermodynamic parameters:

$$\sigma_{ik} = -p\delta_{ik} + 3nT\sum_{\alpha}\left[x^{\alpha}_{ik} - \frac{1}{3}\,\delta_{ik} - \frac{1}{2}(u^{\alpha}_{ik} + u^{\alpha}_{ki})\right], \tag{2}$$

where p is the pressure; n is the number of the molecules in a unit volume; T is the temperature in energy units; $x^{\alpha}_{ik} = 2\mu\lambda_{\alpha}\langle\rho^{\alpha}_{i}\rho^{\alpha}_{k}\rangle/3$, $u^{\alpha}_{ik} = \langle\rho^{\alpha}_{i}T^{\alpha}_{k}\rangle/(3T)$; and averaging is performed over all possible realizations of random force Φ^{α}_{i}.

The thermodynamic variables x^{α}_{ik} introduced in (2) characterize the inertial properties of the macromolecular coil and can, therefore, be used to determine the anisotropy tensor a_{ik}.

According to (7), we write

$$a_{ik} = 6\sum_{\alpha}(x^{\alpha}_{ik} - \delta_{ik}/3)/(\alpha\pi)^{2}.$$

Assuming that the anisotropy in the considered polymer system is characterized by the size and the shape of a macromolecular coil and is, therefore, described by a symmetrical tensor of the second rank a_{ik}; then, for the coefficients B^{α}_{ij} and E^{α}_{ij}, we have

$$\begin{aligned} B^{\alpha}_{ik} &= B\Big(\delta_{ik} + 3\beta\Big(a_{ik} - \frac{a_{jj}}{3}\,\delta_{ik}\Big) + \text{æ}\, a_{jj}\delta_{ik}\Big)^{-1}, \\ E^{\alpha}_{ik} &= E\Big(\delta_{ik} + 3\varepsilon\Big(a_{ik} - \frac{a_{jj}}{3}\,\delta_{ik}\Big) + \nu a_{jj}\delta_{ik}\Big)^{-1}. \end{aligned} \tag{3}$$

Here B and E are the degrees of increase of the friction coefficient ζ for the forces of internal and external friction; β, ε, æ, and ν are the phenomenological constants of microanisotropy, which take into account the size (æ, ν) and the shape (β, ε) of the macromolecular coil in the equation of dynamics of the macromolecule. A comparison of (3) with some other possible approaches is carried out in [10].

This method of accounting for the induced anisotropy generalizes the expression proposed in [9] for the case of large velocity gradients

$$B^{\alpha}_{ik} = B(\delta_{ik} - 3\beta a_{ik}), \quad E^{\alpha}_{ik} = E(\delta_{ik} - 3\varepsilon a_{ik}).$$

The internal thermodynamic variables x^{α}_{ik} and u^{α}_{ik} satisfy the following relaxation equations:

$$\begin{aligned} &\frac{D}{Dt}\,x^{\alpha}_{ik} - \frac{B\tau^{R}_{\alpha}}{\tau_{\alpha}}(x^{\alpha}_{ij}\gamma_{jl}c^{\alpha}_{lk} + x^{\alpha}_{kj}\gamma_{jl}c^{\alpha}_{li}) = -\frac{1}{2\tau_{\alpha}}\Big(\Big(x^{\alpha}_{ij} - \frac{1}{3}\,\delta_{ij}\Big)b^{\alpha}_{jk} + \Big(x^{\alpha}_{kj} - \frac{1}{3}\,\delta_{kj}\Big)b^{\alpha}_{ji}\Big), \\ &\frac{D}{Dt}\,u^{\alpha}_{ik} + \frac{1}{\tau}\,u^{\alpha}_{ik} + \frac{1}{2\tau_{\alpha}}\,b^{\alpha}_{ij}u^{\alpha}_{jk} - \frac{B\tau^{R}_{\alpha}}{\tau_{\alpha}}\,e^{\alpha}_{ij}\gamma_{ik}u^{\alpha}_{ik} = \psi\,\frac{B\tau^{R}_{\alpha}}{\tau\tau_{\alpha}}\Big(\Big(x^{\alpha}_{il} - \frac{1}{3}\,\delta_{il}\Big)d^{\alpha}_{lk} - 2B\tau^{R}_{\alpha}x^{\alpha}_{il}\gamma_{lj}f^{\alpha}_{jk}\Big). \end{aligned} \tag{4}$$

The auxiliary variables used here have the form

$$\tau^{R}_{\alpha} = \zeta/4T\mu\lambda_{\alpha}, \quad \tau_{\alpha} = \tau/2 + \tau^{R}_{\alpha}(B + E),$$

$$\beta_{ij} = 3\beta\Big(a_{il} + \frac{1}{3}\Big(\frac{\text{æ}}{\beta} - 1\Big)a_{ss}\delta_{il}\Big)\Big(\delta_{lj} + 3\beta\Big(a_{lj} + \frac{1}{3}\Big(\frac{\text{æ}}{\beta} - 1\Big)a_{ss}\delta_{lj}\Big)\Big)^{-1},$$

$$\varepsilon_{ij} = 3\varepsilon\Big(a_{il} + \frac{1}{3}\Big(\frac{\nu}{\varepsilon} - 1\Big)a_{ss}\delta_{il}\Big)\Big(\delta_{lj} + 3\varepsilon\Big(a_{lj} + \frac{1}{3}\Big(\frac{\nu}{\varepsilon} - 1\Big)a_{ss}\delta_{lj}\Big)\Big)^{-1},$$

$$b^{\alpha}_{ik} = \Big(\delta_{ik} - \frac{B\tau^{R}_{\alpha}}{\tau_{\alpha}}(\beta_{ik} + \psi\varepsilon_{ik})\Big)^{-1}, \qquad c^{\alpha}_{ik} = (\delta_{ij} - \beta_{ij})b^{\alpha}_{jk},$$

$$e^{\alpha}_{ik} = b^{\alpha}_{ij}(\delta_{jk} - \beta_{jk}), \quad d^{\alpha}_{ik} = b^{\alpha}_{ij}(\delta_{kj} - \varepsilon_{kj}), \quad f^{\alpha}_{ik} = c^{\alpha}_{ij}(\delta_{kj} - \varepsilon_{jk}).$$

Hence, the parameters of the derived rheological model (3) are: $B\tau^{*}$, the maximum relaxation time;

$\chi = \tau/2B\tau^*$, the dimensionless relaxation time; $\psi = E/B$, the degree of internal viscosity; β, ε, æ, and ν, the coefficients of microanisotropy. The influence of these parameters on the solutions of system of Eqs. (2) and (4) was considered in [6–10]. In this case, estimates for the parameters $\chi \ll 1$ [5, 9], $\psi \ll 1$ [7] and $\beta \ll 1$ were obtained in [8–10]. The parameters χ and ψ happened to be responsible for the linear viscoelasticity, while the coefficients of microanisotropy manifest themselves in the nonlinear region.

The Zeroth-Approximation Models. The written system of equations is rather complex. Therefore, zeroth- and first- approximation models were formulated earlier in [5], making use of the smallness of parameters χ and ψ. The obtained results in this case make it necessary to consider the zeroth-approximation models for χ and ψ more carefully. In this case $u^\alpha_{ik} = 0$, and Eqs. (2) and (4) take the form

$$\begin{gathered}\sigma_{ik} = -p\delta_{ik} + 3nT\sum_\alpha \Big(x^\alpha_{ik} - \frac{1}{3}\,\delta_{ik}\Big),\\ \frac{d}{dt}\,x^\alpha_{ik} - \nu_{ij}x^\alpha_{jk} - \nu_{kj}x^\alpha_{ji} = -\frac{1 + (\ae - \beta)a_{ss}}{B\tau^R_\alpha}\Big(x^\alpha_{ik} - \frac{1}{3}\,\delta_{ik}\Big) - \frac{3\beta}{2B\tau^R_\alpha}\Big(\Big(x^\alpha_{ij} - \frac{1}{3}\,\delta_{ij}\Big)a_{jk} + \Big(x^\alpha_{kj} - \frac{1}{3}\,\delta_{kj}\Big)a_{ji}\Big),\end{gathered} \tag{5}$$

where a_{ss} is the trace of the anisotropy tensor a_{ik}. The parameters of this system of equations will then be $B\tau^*$, β, and æ.

The parameter $B\tau^*$ can be determined through the initial shear viscosity $\eta_0 = (\pi^2/6)nTB\tau^*$, and, therefore, it becomes possibile to study the influence of the anisotropy parameters β and æ on the solutions to system of Eqs. (5). Considering the stationary shear flow, when only one component of the tensor of velocity gradients, ν_{12}, is nonzero, we obtain from (5) the following expressions for the nonzero components of the stress tensor σ_{ik} with third-order accuracy with respect to ν_{12}:

$$\begin{gathered}\sigma_{11} + p = \frac{\pi^4}{45}\Big(1 - \frac{\beta}{2}\Big)nT(B\tau^*\nu_{12})^2, \quad \sigma_{22} + p = -\frac{\pi^4}{90}\,\beta nT(B\tau^*\nu_{12})^2,\\ \sigma_{12} = \frac{\pi^2}{6}\,nT\Big[B\tau^*\nu_{12} - \Big(\frac{24\pi^4}{1575}\,\beta + \frac{4\pi^4}{945}(\ae - \beta)(B\tau^*\nu_{12})^3\Big)\Big].\end{gathered} \tag{6}$$

Hence, the parameters æ and β are responsible for the nonlinear properties of system (4), and in the case of simple shear, the parameter β manifests itself already in the second order with respect to the velocity gradients, but æ only in the third.

From (6) we find expressions for the viscosimetric functions

$$\Psi_1 = \frac{\sigma_{11} - \sigma_{22}}{(\nu_{12})^2} = \frac{\pi^4}{45}\,nT, \quad \Psi_2 = \frac{\sigma_{22} - \sigma_{33}}{(\nu_{12})^2} = -\frac{\pi^4}{90}\,\beta nT, \quad \eta = \frac{\sigma_{12}}{\nu_{12}} = \eta_0\Big[1 - \frac{4\pi^4}{105}\,\Big(\frac{2}{5}\,\beta + \frac{\ae - \beta}{9}\Big)(B\tau^*)^2\Big].$$

The results obtained here differ at $\ae = 0$ from the results in [9] because of a misprint which was the fault of the authors.

In the case of a dumb-bell model ($N = 1$), system of Eqs. (5) has the form

$$\sigma_{ik} = -p\delta_{ik} + \frac{3\eta_0}{\tau_0}\,a_{ik}, \quad \frac{d}{dt}\,a_{ik} - \nu_{ij}a_{jk} - \nu_{kj}a_{ji} + \frac{1 + (\ae - \beta)I}{\tau_0}\,a_{ik} = \frac{2}{3}\,\gamma_{ik} - \frac{3\beta}{\tau_0}\,a_{ij}a_{jk}. \tag{7}$$

Here η_0 and τ_0 are the initial shear viscosity and relaxation time; $I = a_{ss}$. Hence, under the assumption of isotropic relaxation ($\beta = 0$), we come to the well-known Pokrovsky structural–phenomenological model. If $\beta = \ae$, the coefficients in Eq. (7) do not depend on the first invariant of the tensor a_{ik}, which corresponds to the case studied in [12, 13].

Nonlinear Stationary Effects with Simple Shear and Uniaxial Extension. Considering the nonlinear effects in a stationary shear flow, system of Eqs. (7) takes the form

$$a_{11} = 2\tau_N s a_{12} - 3\beta\tau_N(a^2_{11} + a^2_{12}), \quad a_{22} = -3\beta\tau_N(a^2_{22} + a^2_{12}), \quad a_{12} = \frac{\tau_N}{3}s + \tau_N s a_{22} - 3\beta\tau_N a_{12}(a_{11} + a_{22}), \tag{8}$$

where $\tau_N = 1/(1 + (\ae - \beta)I)$; $I = a_{11} + a_{22}$; $s = \tau_0\nu_{12}$.

The results of computations of the viscosimetric functions from system of Eqs. (8) are given in Figs. 1–5. In Figs. 1 and 2, the relation between the stationary shear viscosity η and the dimensionless velocity of

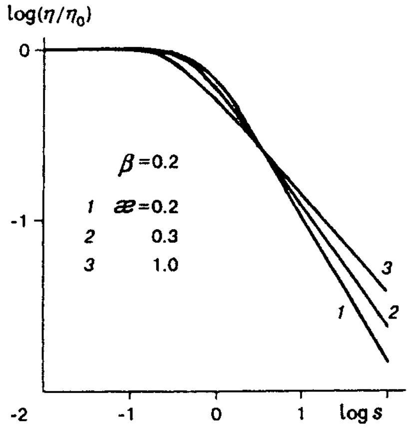

Fig. 1

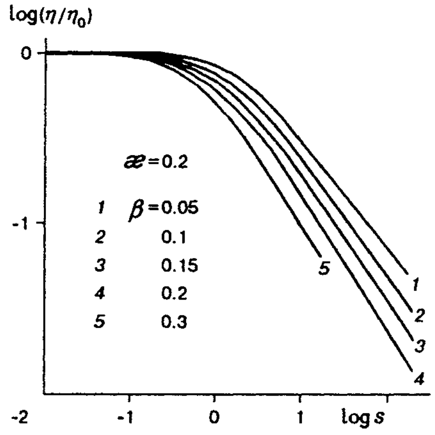

Fig. 2

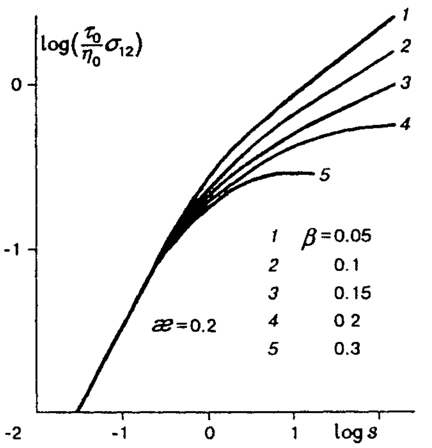

Fig. 3

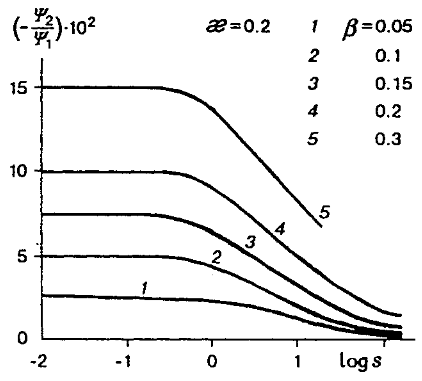

Fig. 4

shear s is presented. One can see that an increase in β leads to a decrease in η, and an increase in æ (at fixed β) leads to an increase in η. In this case, the influence of β is the more significant (a variation of β of from 0.1 to 0.15 is "compensated" by a variation of æ of from 0.3 to 1).

In Fig. 3, the flow curve that represents the relation between the shear stress σ_{12} and the velocity of shear is shown. At æ $> \beta$, σ_{12} is an ascending function of shear velocity ν_{12}, which agrees well with the experimental data from [14].

In Fig. 4, the ratio between the second and the first remainders of the normal stresses $(\sigma_{22}-\sigma_{33})/(\sigma_{11}-\sigma_{22}) = \Psi_2/\Psi_1$ is shown. This ratio is negative and small in absolute value. The parameter β significantly influences this ratio, while the æ influence is negligible. The parameter æ also does not influence the coefficient of the first remainder of the normal stresses Ψ_1, which is presented in Fig. 5.

For stationary uniaxial extension, system of Eqs. (7) has the form

$$3\beta\tau_N s b_{11}^2 + (1-2\tau_N s)b_{11} = \frac{2}{3}\tau_N, \quad 3\beta\tau_N s b_{22}^2 + (1+\tau_N s)b_{22} = -\frac{1}{3}\tau_N$$

$$[I = (b_{11}+2b_{22})s, \quad s = \tau_0\nu_{11}, \quad b_{ii} = a_{ii}/s].$$

In this case, the behavior of the polymer liquid is characterized by a stationary viscosity with extension $\lambda = (\sigma_{11}-\sigma_{22})/\nu_{11}$, the dependence of which on the dimensionless velocity of extension s at different values of the parameter $\beta =$ æ is given in Fig. 6. One can see that at high velocities of extension s, the coefficient of

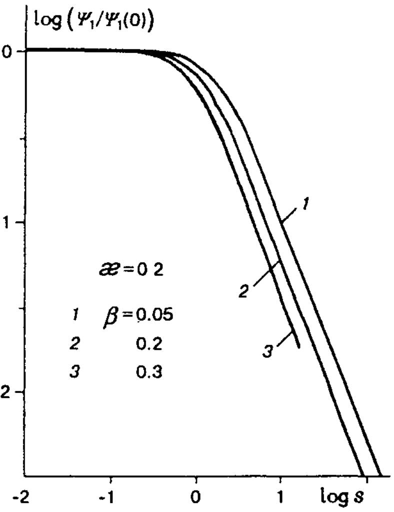

Fig. 5

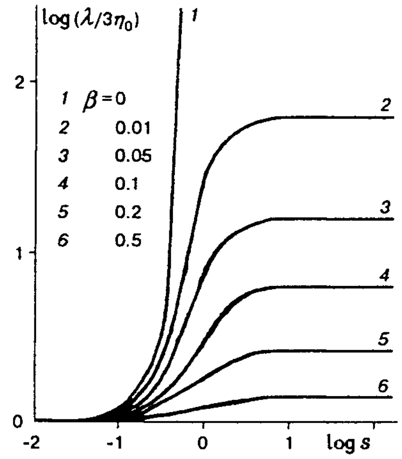

Fig. 6

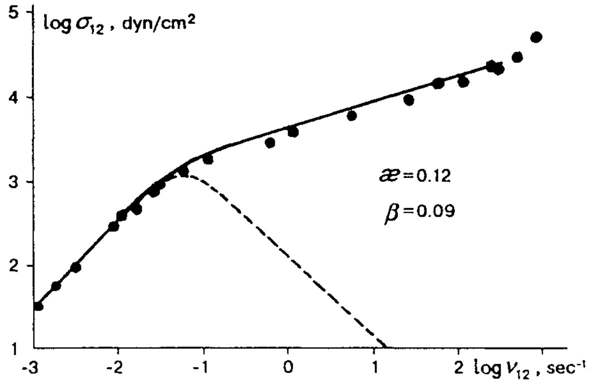

Fig. 7

viscosity λ reaches a stationary value, which is in agreement with the calculations from [3, 12].

In Fig. 7, a comparison of the experimental data for the flow curve of a 12% polyisobutilene solution in decaline obtained in [14] with calculations by system of Eqs. (8) (solid line) and by the system of first-order-approximation equations from [7] (dotted line) is given.

The presented results show the validity of models (5) and (7) for the description of stationary nonlinear effects in linear polymers with simple shear and uniaxial extension. Thus, we can recommend these models as initial approximations for construction of a sequence of rheological constitutive relations. At the same time, when passing from the general system (2), (4) to the first-order-approximation model, the properties of the model can deteriorate. Therefore, the statement of the first-order-approximation model apparently requires an improvement in the initial equations of macromolecule dynamics.

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