

STRUCTURAL-KINETIC APPROACH IN THE THEORY OF FLOWS OF POLYMER SOLUTIONS AND MELTS. NONLINEAR EFFECTS IN SIMPLE SHEAR

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This paper is a continuation of [1], where, based on microstructural concepts, a rheological equation of state (RES) is derived and some relations of linear viscoelasticity are considered. The results of [1] show good agreement with experimental data on the dynamic shear modulus for monodisperse polymer solutions and melts. This raises the question as to whether nonlinear effects in flows of polymer systems can be described using the rheological model of [1]. However, the solution of this problem requires the refinement of some relations obtained previously.

Based on the equations of the dynamics of a macromolecule [1, 2], the expression for the stress tensor of a polymer system is of the form

$$\sigma_{ik} = -p_0 \delta_{ik} + 3nT \sum_{\alpha} \left(x_{ik}^{\alpha} - \frac{1}{3} \delta_{ik} - \frac{1}{2} (u_{ik}^{\alpha} + u_{ki}^{\alpha}) \right). \tag{1}$$

For the dimensionless tensors x_{ik}^{α} and u_{ik}^{α} entering into (1), the relaxation equations obtained in [1] are of the form

$$\frac{D}{Dt} x_{ik}^{\alpha} - x_{ij}^{\alpha} \gamma_{jn} c_{nk}^{\alpha} - x_{kj}^{\alpha} \gamma_{jn} c_{ni}^{\alpha} = -\frac{1}{2B\tau_{\alpha}^R} \left(\left(x_{ij}^{\alpha} - \frac{1}{3} \delta_{ij} \right) b_{jk}^{\alpha} + \left(x_{kj}^{\alpha} - \frac{1}{3} \delta_{kj} \right) b_{ji}^{\alpha} \right); \tag{2}$$

$$\frac{D}{Dt} u_{ik}^{\alpha} - c_{ij}^{\alpha} \gamma_{jn} u_{kn}^{\alpha} + \frac{1}{2B\tau_{\alpha}^R} c_{ij}^{\alpha} u_{jk}^{\alpha} + \frac{1}{\tau} u_{ik}^{\alpha} = \frac{\psi}{\tau} \left(\left(x_{ij}^{\alpha} - \frac{1}{3} \delta_{ij} \right) f_{jk}^{\alpha} - 2B\tau_{\alpha}^R x_{ij}^{\alpha} \gamma_{jn} d_n^{\alpha} \right). \tag{3}$$

Here

$$b_{ik}^{\alpha} = \left(\frac{\tau}{2B\tau_{\alpha}^R} \delta_{ik} + \beta_{ik}^0 + \psi \epsilon_{ik}^0 \right)^{-1}; \quad c_{ik}^{\alpha} = \beta_{ij}^0 b_{jk}^{\alpha}; \quad f_{ik}^{\alpha} = b_{ij}^{\alpha} \epsilon_{kj}^0;$$

$$\beta_{ik}^0 = \left(\delta_{ik} + 3\beta \left(a_{ik} - \frac{a_{jj}}{3} \delta_{ik} \right) + \varkappa a_{jj} \delta_{ik} \right)^{-1}; \quad \epsilon_{ik}^0 = \left(\delta_{ik} + 3\varepsilon \left(a_{ik} - \frac{a_{jj}}{3} \delta_{ik} \right) + \nu a_{jj} \delta_{ik} \right)^{-1};$$

$$a_{ik} = 6 \sum_{\alpha} (x_{ik}^{\alpha} - \delta_{ik}/3) / (\alpha \pi^2); \quad \frac{D}{Dt} x_{ik}^{\alpha} = \frac{d}{dt} x_{ik}^{\alpha} - \omega_{ij} x_{jk}^{\alpha} - \omega_{kj} x_{ij}^{\alpha}$$

is the Yauman derivative of the tensor quantity x_{ik}^{α} , τ is the relation time of the environment, $B\tau_{\alpha}^R = B\tau^*/\alpha^2$ are the Rouse relaxation times, ψ is a measure of intrinsic viscosity, γ_{ij} and ω_{ij} are the symmetric and antisymmetric parts of the velocity-gradient tensor ν_{ij} , the quantities β , \varkappa , ε , and ν are the induced anisotropy parameters, and δ_{ik} is the Kronecker delta.

Since the expression for the stress tensor (1) is written in symmetric form, it is more convenient to use the equation $y_{ik}^{\alpha} = (u_{ik}^{\alpha} + u_{ki}^{\alpha})/2$ instead of (3). This equation can be obtained from (3) using the symmetry of the tensors c_{ik}^{α} and b_{ik}^{α} and assuming the permutability of the tensors u_{ik}^{α} with γ_{ik} , c_{ik}^{α} , and b_{ik}^{α} . By virtue of the existence of a functional relationship between x_{ik}^{α} , u_{ik}^{α} , and γ_{ik} and also by virtue of the fact that c_{ik}^{α} and b_{ik}^{α} are expressed in terms of x_{ik}^{α} , this assumption is not a significant constraint.

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Then, instead of (1) and (3), we obtain

$$\sigma_{ik} = -p_0 \delta_{ik} + 3nT \sum_{\alpha} \left(x_{ik}^{\alpha} - \frac{1}{3} \delta_{ik} - y_{ik}^{\alpha} \right); \quad (4)$$

$$\begin{aligned} & \frac{D}{Dt} y_{ik}^{\alpha} - \frac{1}{2} (c_{ij}^{\alpha} \gamma_{jn} y_{kn}^{\alpha} + c_{kj}^{\alpha} \gamma_{jn} y_{ni}^{\alpha}) + \frac{1}{4B\tau_{\alpha}^R} (b_{ij}^{\alpha} y_{jk}^{\alpha} + b_{kj}^{\alpha} y_{ji}^{\alpha}) + \frac{1}{\tau} y_{ik}^{\alpha} \\ &= \frac{\psi}{2\tau} \left(\left(x_{ij}^{\alpha} - \frac{1}{3} \delta_{ij} \right) f_{jk}^{\alpha} - 2B\tau_{\alpha}^R x_{ij}^{\alpha} \gamma_{jn} d_{nk}^{\alpha} + \left(x_{kj}^{\alpha} - \frac{1}{3} \delta_{kj} \right) f_{ji}^{\alpha} - 2B\tau_{\alpha}^R x_{kj}^{\alpha} \gamma_{jn} d_{ni}^{\alpha} \right). \end{aligned} \quad (5)$$

System (2), (4), and (5) describes a nonlinear viscoelastic anisotropic fluid and is characterized by six dimensionless parameters, $\chi = \tau/2B\tau^*$, ψ , β , ε , \varkappa , and ν , and by two dimensional parameters, $B\tau^*$ and nT .

RES (2), (4), and (5) should be checked for correspondence to real polymer fluid flows. The flows realizable in practice are very diverse, and, naturally, the check of the RES should be begun with the simplest cases. One type of flows that are often realized in viscometers of various design is simple shear. In this case, the velocity-gradient tensor contains only one nonzero component $\nu_{12}(t)$, which varies with time by a known law.

The rheological behavior of the polymer system is then conveniently characterized by the following viscometric functions: the shear viscosity η and the first N_1 and second N_2 differences of normal stresses, which are given by

$$\eta = \sigma_{12}/\nu_{12}, \quad N_1 = \sigma_{11} - \sigma_{22}, \quad N_2 = \sigma_{22} - \sigma_{33} \quad (6)$$

and are generally functions of the velocity gradient and time.

The dependence $\nu_{12}(t)$ is often used in the form $\nu_{12}(t) = \gamma E(t)$ or $\nu_{12}(t) = \gamma E(-t)$. Here γ is the shear velocity and $E(t)$ is the unit Heaviside function. In the first case, system (2), (4), and (5) describes the establishment of stresses from the state of rest, and the corresponding viscometric functions (6) are denoted by $\eta^+(\gamma, t)$ and $N_1^+(\gamma, t)$. In the second case, this system describes stress relaxation after shear deformation, and functions (6) are denoted by $\eta^-(\gamma, t)$ and $N_1^-(\gamma, t)$.

We first consider the following stationary quantities:

$$\eta(\gamma) = \lim_{t \rightarrow \infty} \eta^+(\gamma, t), \quad N_1(\gamma) = \lim_{t \rightarrow \infty} N_1^+(\gamma, t). \quad (7)$$

At low shear velocities, the second difference of normal stresses N_2 is given by the formula

$$N_2 = -\left(\frac{15}{2\pi^2} \chi + \frac{1}{2} \beta \right) N_1, \quad (8)$$

obtained by Pokrovskii and Pyshnograï [3]. The calculations in [3] show that, for $\psi \ll 1$, formula (8) remains valid for $\gamma B\tau^* < 10$. From analysis of various experimental data, Ramachandran [4] concluded that the ratio N_2/N_1 is negative and depends neither on the concentration c nor on the molecular weight M of the polymer ($N_2/N_1 < 0.3$). Since χ is known [1-3] to depend on M , it follows from the aforesaid that the anisotropy parameter β must depend neither on c nor on M and the estimate $\chi \ll \beta < 1$ must hold.

To compare RES (2), (4), and (5) with experiments, we use the data of Menezes and Graessley [5], who studied shear flows of solutions of polybutadiene with various molecular weights. It is convenient to use their results, because their data on linear viscoelasticity have already been compared with (2), (4), and (5) in [1]. From this comparison, the following estimates of the parameters of the rheological model (2), (4), and (5) were obtained: $\chi = 0.077, 0.025, 0.011$, and 0.005 , $B\tau^* = 0.21, 2.35, 16.27$, and 147 sec, and $nT = 840.4, 480.2, 321.5, 206.7$ Pa for molecular weights $M = 2 \cdot 10^5, 3.4 \cdot 10^5, 5.17 \cdot 10^5$, and $8.13 \cdot 10^5$, respectively; in all cases, $\psi = 0.025$.

The results of the calculation of the experimental functions (7) and the corresponding experimental values are given in Fig. 1. In the calculations, we used the following induced anisotropy parameters: $\varkappa = 0.1$, $\beta = 0.25$, $\varepsilon = 0$, and $\nu = 0.1$. They were chosen from the condition of the best agreement between the theoretical curves and the experimental data. The value of N_2 was not measured in [5].

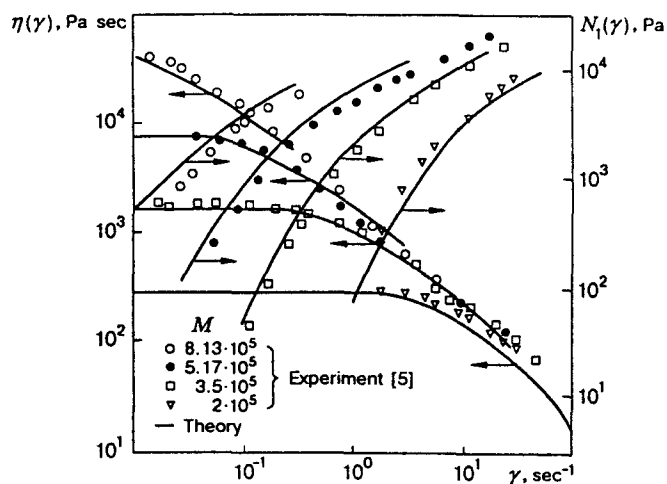


Fig. 1

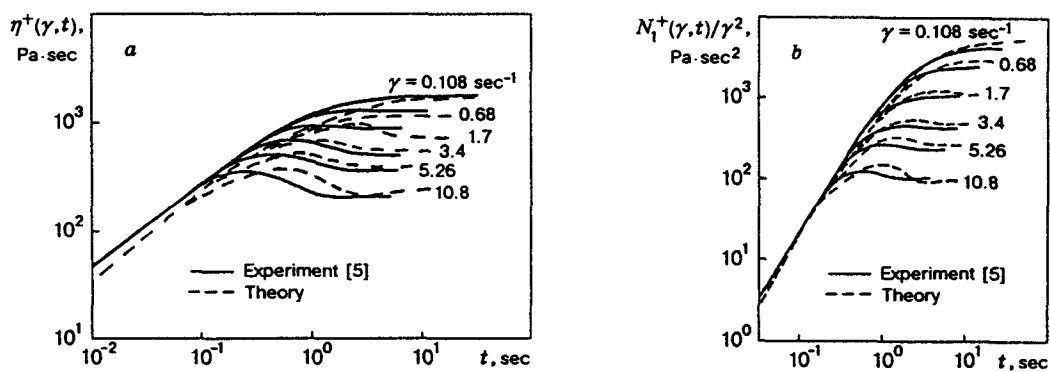


Fig. 2

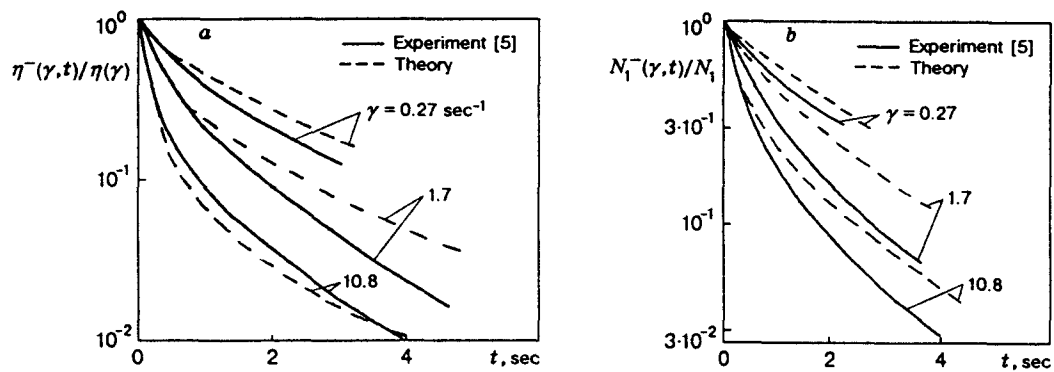


Fig. 3

Let us consider nonlinear unsteady effects. The results of the calculation of the establishment of stresses for a specimen with $M = 3.5 \cdot 10^5$ are given in Fig. 2, which shows that Eqs. (2), (4), and (5) describes the nonmonotonic attainment of $\eta^+(\gamma, t)$ and $N_1^+(\gamma, t)$ at high shear velocities. It is also found that $\eta^+(\gamma, t) \sim t$ (Fig. 2a) and $N_1^+(j, t) \sim t^2$ (Fig. 2b) at small t .

The data for $\eta^-(\gamma, t)$ and $N_1^-(\gamma, t)$ are given in Fig. 3a and b, which show that (2), (4), and (5) confirm the presence of two characteristic times for stress relaxation after intense shear deformation. The anisotropy parameter values are the same as in Fig. 1.

Thus, for the first time, we obtained a RES that is applicable for the description of steady and unsteady effects in the linear and nonlinear regions of strain rates and more complex flow regimes of linear polymer solutions and melts.

REFERENCES

1. G. V. Pyshnograï, "Structural-kinetic approach in the theory of flows of linear-polymer solutions and melts," *Prikl. Mekh. Tekh. Fiz.*, **38**, No. 3, 122–130 (1997).
2. Yu. A. Altukhov and G. V. Pyshnograï, "The microstructural approach in the theory of linear-polymer flows and associated nonlinear effects," *Vysokomol. Soed., Ser. A*, No. 9, 1–9 (1996).
3. V. N. Pokrovskii and G. V. Pyshnograï, "Nonlinear effects in the dynamics of concentrated polymer solutions and melts," *Izv. Akad. Nauk SSSR, Mekh. Zhidk. Gaza*, No. 4, 88–96 (1990).
4. S. Ramachandran, H. W. Gao, and E. B. Christiansen, "Dependence of viscoelastic flow functions on molecular structure for linear and branched polymers," *Macromolecules*, **18**, 695–699 (1985).
5. E. V. Menezes and W. W. Graessley, "Nonlinear rheological behavior of polymer systems for several shear-flow histories," *J. Polym. Sci., B, Polym. Phys.*, **20**, 1817–1833 (1982).