

The Mesoscopic Constitutive Equations for Polymeric Fluids and Some Examples of Viscometric Flows*

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ABSTRACT

Constitutive equations for melts and concentrated solutions of linear polymers are derived as consequences of dynamics of a separate macromolecule. The model is investigated for viscometric flows. It was shown that the model gives a good description of non-linear effects of simple shear polymer flows: viscosity anomalies, first and second normal stresses, non-steady shear stresses.

Keywords: Rheology; Linear Polymer Melts and Solutions; Constitutive Equation; Mesoscopic Approach

1. Introduction

Describing viscoelastic behavior of the polymer system, one should distinguish the case of highly concentrated ($c > 10\%$) solutions and melts of long polymers—strongly entangled systems ($M > 10M_e$), where M is the length (in any units) of a macromolecule and M_e is the length of a part of macromolecule between the adjacent entanglements [1-3], and the case of melts of shorter polymers and half-dilute polymer solutions ($c \sim 1\% - 10\%$)—weakly entangled systems ($M < 10M_e$) [4]. The convenient characteristic of a system of entangled linear macromolecules (solutions and melts of polymers) appears to be $\chi = \pi^2 \rho^2 M_e / (12Mc^2)$, which, for strongly entangled systems, is inversely proportional to number of entanglements for one macromolecule— M/M_e . Here ρ is the polymer density. The quantity χ can be easily with estimated the value G_e of real component of dynamic modulus $G'(\omega)$ on the typical plateau, according to the formula for weakly and strongly entangled systems, correspondingly

$$G'_p \sim \chi^{-1/2}, G'_p \sim \chi^{-1}.$$

In this paper we consider the case of weakly entangled systems and formulate a rheological equation of state (RES) that establishes a relationship between the stress tensor, kinetic characteristics, and internal dynamic parameters. At present, a large number of such equations of various complexity is known for polymeric liquids, but,

despite various approaches both phenomenological [5-7] and microstructural [1,2,8-11] ones, the problem how to include specific features of a polymer system into the form of constitutive equations has no complete solution. This is due to both complexity of these systems, which are formed by tangled macromolecules, and mathematical difficulties [11]. The information about the microstructure and micro dynamics of the material ought to be incorporated into the present theory of linear and nonlinear relaxation phenomena in polymer systems. An advantage of the micro structural approach is a possibility of studying the relationship between the micro characteristics of a polymer system (concentration and molecular weight of the polymer) and macroscopically observed quantities (viscosity, shear and normal stresses, etc.). In this connection using microstructural concepts it's feasible to formulate a sequence of RES that takes into account new molecular effects in each stage. At [4,9,12] obtained and studied a simple rheological model which can be chosen as an initial approximation in formulating such a sequence of RES. In this work, RES [4] is extended to the case of allowance for the additional corrections caused by intrinsic viscosity and the delayed interaction of a macromolecule with its environment. Realization of this approach involves consequent solution of two problems: formulation of the equations of dynamics for a macromolecule and transition from the formulated equations to RES. The resulting equations can be recommended as the first approximation in constructing a sequence of RES. Comparison of the approach with others, Graessley [1,3] and Doi-Edwards [8] approaches, one

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can find in [9,12].

2. Dynamics of a Macromolecule in Flow

The mesoscopic approach to the description of the dynamics of polymer systems is based on the equations of the macromolecule dynamics which cannot be formulated without additional assumptions, namely:

1) A monomolecular approximation of the system. It means that, instead of the entire set of interacting macromolecules in the volume we consider are non-interacting separate macromolecule, moving in the effective medium formed by the solvent and the other macromolecules.

2) The coarse-grained approximation of a macromolecule. It means that, irrespective of the chemical nature of the polymer, the slow motions of the chosen macromolecule can be described as motions of N centers of friction (beads) connected by elastic entropy forces (springs) in a chain. These assumptions lead to the following equations of the macromolecules dynamics [9] in normal modes:

$$m \frac{d}{dt} \psi_i^\alpha = -\zeta (\psi_i^\alpha - v_{ij} \rho_j^\alpha) + \Gamma_i^\alpha + T_i^\alpha - 2T \mu \lambda_\alpha \rho_i^\alpha + \Phi_i^\alpha, \quad (1)$$

where ρ_i^α and ψ_i^α are the i -th components of the normal coordinates and velocity, m is the mass of a bead. Here ζ is the friction coefficient of a bead in a monomer fluid, v_{ij} is the velocity-gradient tensor, which is conveniently expressed below as the sum of symmetric γ_{ij} and anti-symmetric ω_{ij} parts, and the bracketed expression is the difference between the particle velocity at a given point of space and the velocity of undisturbed flow at this point. The force Γ_i^α describes the interaction of the polymer chain with the environment via the solvent, while the force T_i^α is an intrinsic resistance force, Φ_i^α is a random force, and $2T \mu \lambda_\alpha$ is the coefficient of elasticity.

Expression (1) is the basis for the description of the dynamics for different polymer systems [12]. The definition of the extra forces Γ_i^α and T_i^α allows one to specify the polymer system. Different models of these forces correspond to different physical cases. For dilute polymer solutions, in which polymer macromolecules can be considered non-interacting, the extra forces are considered to be equal to zero [9]. In concentrated polymer systems, the macromolecules cannot be considered as not interacting. So, one has to take into account the reaction of the environment and the strengthening of the friction coefficient. The first factor is due to the delayed character of interaction of the macromolecule with its environment, and the second is due to the fact that the

chosen bead undergoes resistance not only from the monomer solvent, but also from other macromolecules. Furthermore, one should take into account that, in the flow with nonzero velocity gradients, a macromolecular coil changes its form, and the medium, formed by the coils becomes anisotropic. This mobility anisotropy of beads is called induced and is determined by the shape and orientation of macromolecular coils [4,9,12]. According to all these factors the equation for the force of hydrodynamic entrainment follows:

$$\tau \left(\frac{d}{dt} \Gamma_i^\alpha - \omega_{ij} \Gamma_j^\alpha - p \gamma_{ij} \Gamma_j^\alpha \right) + \Gamma_i^\alpha = -\zeta B \beta_{ij}^0 (\psi_j^\alpha - v_{jn} \rho_n^\alpha) \quad (2)$$

Here τ is the relaxation time of the environment, β_{ij}^0 is the dimensionless tensor friction coefficient of a bead, B is the strengthening measure of the friction coefficient ζ , and p is a parameter. The bracketed expression on the left side of (2) is a substantial derivative of the vector quantity Γ_i^α [9]. The presence of this derivative allows one to meet the principle of material objectivity in Equation (2) [6,9]. Numerical parameter p entering into the definition of the substantial derivative can take different values. For $p = 0$, the substantial derivative becomes the Jaumann derivative which has a simpler form while for $p = 1$ and -1 , it becomes the upper and lower convective derivatives, respectively. The specific value of p corresponding to one of the above-mentioned derivatives in (2) is determined below.

If macromolecules form a tangled system besides the force of hydrodynamic entrainment, one should take into account the intrinsic viscous force T_i^α , the meaning of which is elucidated by Pokrovskii *et al.* [12]. The specific requirement imposed on the force T_i^α is that this force is vanishing when a macromolecular coil is rotating as a unit. All this allows one to write the equation for this force in similar to (2) manner in the form

$$\tau \left(\frac{d}{dt} T_i^\alpha - \omega_{ij} T_j^\alpha - p \gamma_{ij} T_j^\alpha \right) + T_i^\alpha = -\zeta E \varepsilon_{ij}^0 (\psi_j^\alpha - \omega_{jn} \rho_n^\alpha) \quad (3)$$

where: ε_{ij}^0 is the dimensionless tensor friction coefficient and E is the strengthening measure of the friction coefficient ζ for the intrinsic viscous force T_i^α . Intrinsic viscous force T_i^α (since Γ_i^α) has relaxation character and depends on the anisotropic properties of the environment.

We assume that the anisotropy of mobility in considered polymer system is characterized by the second-order symmetric tensor a_{ik} . Then, for coefficients β_{ij}^0 and ε_{ij}^0 we write [9]

$$\begin{aligned}\beta_{ik}^0 &= \left(\delta_{ik} + 3\beta \left(a_{ik} - \frac{a_{ij}}{3} \delta_{ik} \right) + \kappa a_{ij} \delta_{ik} \right)^{-1}, \\ \varepsilon_{ik}^0 &= \left(\delta_{ik} + 3\varepsilon \left(a_{ik} - \frac{a_{ij}}{3} \delta_{ik} \right) + \nu a_{ij} \delta_{ik} \right)^{-1}.\end{aligned}\quad (4)$$

Thus, (1-4) is the system of equations of dynamics of a macromolecule. The random force $\Phi_i^\alpha(t)$ entering into (1) is the Gaussian random process with a zero average. Its correlation tensor satisfies the corresponding fluctuation-dissipation relation [9,10].

3. Stress Tensor and Rheological Equation of State

Equations (1)-(4) give a microscopic picture of a polymer system flow based on discrete variables. Transition to the continuous case, *i.e.*, to the description of polymer-system flows in terms of continuum mechanics, requires introduction of macroscopic variables—density $\rho(x,t)$ and momentum density $\rho v(x,t)$. These variables are introduced in the standard manner [9,11]:

$$\begin{aligned}\rho(x,t) &= \sum m \langle \delta(x-r^\alpha) \rangle, \\ \rho v(x,t) &= \sum m \langle u^\alpha \delta(x-r^\alpha) \rangle.\end{aligned}\quad (5)$$

Here r^α and u^α are vectors of position and velocity of the bead with number α , x is the co-ordinate vector of the chosen point in space, and t is time. Sum is taken over all beads in a unit volume, and averaging is performed over the ensemble of all possible realizations of the random force $\Phi_i^\alpha(t)$.

Differentiating (5) due to time yields an equation of mass conservation, and transformation to generalized coordinates using (1) yields an equation for momentum density. In the latter case, we have an expression for the stress tensor of a polymer system in terms of statistical characteristics of the system (1-4) solutions:

$$\begin{aligned}\sigma_{ik} &= -p_0 \delta_{ik} \\ &+ 3nT \sum_\alpha \left[x_{ik}^\alpha - \frac{1}{3} \delta_{ik} - \frac{1}{2} (u_{ik}^\alpha + u_{ki}^\alpha) \right],\end{aligned}\quad (6)$$

where p_0 is pressure, n is the number of macromolecules in a volume unit, T is the temperature in energy units, and $x_{ik}^\alpha = 2\mu\lambda_\alpha \langle \rho_i^\alpha \rho_k^\alpha \rangle / 3$ and $u_{ik}^\alpha = \langle \rho_i^\alpha T_k^\alpha \rangle / (3T)$ are internal thermodynamic parameters with equilibrium values

$$x_{ik}^\alpha = \frac{1}{3} \delta_{ik}, \quad u_{ik}^\alpha = 0 \quad (7)$$

In the inertia-free case ($m = 0$), one can formulate (see Appendix) the relaxation equations for the dimensionless correlation moments x_{ik}^α and u_{ik}^α in the following form

$$\begin{aligned}\frac{D}{Dt} x_{ik}^\alpha - x_{ij}^\alpha \gamma_{jn} c_{nk}^\alpha - x_{kn}^\alpha \gamma_{jn} c_{ni}^\alpha \\ = -\frac{1}{2B\tau_\alpha^R} \left(\left(x_{ik}^\alpha - \frac{1}{3} \delta_{ik} \right) b_{jk}^\alpha + \left(x_{kj}^\alpha - \frac{1}{3} \delta_{kj} \right) b_{ji}^\alpha \right), \\ \frac{D}{Dt} u_{ik}^\alpha - p\gamma_{kj} u_{ij}^\alpha - c_{ij}^\alpha \gamma_{jn} u_{kn}^\alpha + \frac{1}{2B\tau_\alpha^R} c_{ij}^\alpha u_{jk}^\alpha + \frac{1}{\tau} u_{ik}^\alpha \\ = \frac{\psi}{\tau} \left(\left(x_{ij}^\alpha - \frac{1}{3} \delta_{ij} \right) f_{jk}^\alpha - 2B\tau_\alpha^R x_{ij}^\alpha \gamma_{jn} d_n^\alpha \right),\end{aligned}\quad (8)$$

where: $\frac{D}{Dt} x_{ik}^\alpha = \frac{d}{dt} x_{ik}^\alpha - \omega_{ij} x_{jk}^\alpha - \omega_{kj} x_{ij}^\alpha$ is the Jaumann derivative of the tensor quantity x_{ik}^α and $\psi = E/B$ is the measure of intrinsic viscosity, $\tau_\alpha^R = \zeta / (4T\mu\lambda_\alpha) = \tau^* / \alpha^2$ is a set of the Rouse relaxation times. In Equations (8)-(9) symbols $b_{ik}^\alpha, c_{ik}^\alpha, f_{ik}^\alpha, d_{ik}^\alpha$ are used.

$$\begin{aligned}b_{ik}^\alpha &= \left(\frac{\tau}{2B\tau_\alpha^R} \delta_{ik} + \beta_{ik}^0 + \psi \varepsilon_{ik}^0 \right)^{-1}; \\ c_{ik}^\alpha &= \left(p \frac{\tau}{2B\tau_\alpha^R} \delta_{ij} + \beta_{ij}^0 \right) b_{jk}^\alpha; \\ (f_{ik}^\alpha &= b_{ij}^\alpha \varepsilon_{kj}^0, \quad d_{ik}^\alpha = c_{ij}^\alpha \varepsilon_{kj}^0)\end{aligned}\quad (10)$$

Thermodynamic variables x_{ik}^α entering into (6) characterize the inertial properties of a macromolecular coil and, hence, can be used to determine anisotropy tensor a_{ik} in (4). Following [9], we write

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

Therefore it becomes possible to establish the physical meaning of the microanisotropy parameters entering into (4). These parameters take into account dimensions (κ, ν) and shape (β, ε) of a macromolecular coil in the equations for macromolecule dynamics.

The Equations (6), (8), and (9) define a nonlinear, anisotropic, viscoelastic fluid. The behavior of system (6), (8), and (9) is determined by the six dimensionless parameters ($\chi = \tau/2B\tau^*$, ψ , β , ε , κ , and ν) and two dimensional parameters ($B\tau^*$ and nT). Parameter χ characterizing the ratio of the relaxation time of the environment τ to the maximum relaxation time $B\tau^*$ was estimated in [9], where it was shown that $\chi \ll 1$ for sufficiently long polymer chains. As to parameter ψ , here two cases can be distinguished: $\psi \ll 1$ [13,14-16] and $\psi \gg 1$ [5], which are discussed below. As in [13], it is convenient to consider simpler forms of equations (8) and (9) by using the smallness of the parameters χ and ψ . We consider in more detail the case $\psi \ll 1$, which corresponds to the dynamics of polymer solutions at a concentration about of 1%.

Considering only effects of the first order with respect

to χ and ψ , we note that Equations (6) and (8) do not change, and Equation (9) takes the form

$$\begin{aligned} & \frac{D}{Dt} u_{ik}^\alpha - \gamma_{ij} u_{jk}^\alpha - p \gamma_{kj} u_{ji}^\alpha \\ &= -\frac{1}{2B\tau_\alpha^R} (\beta_{ij}^0)^{-1} u_{jk}^\alpha - \frac{1}{\tau} u_{ik}^\alpha \\ & - \frac{\psi}{\tau} \left(\left(x_{ij}^\alpha - \frac{1}{3} \delta_{ij} \right) (\beta_{jn}^0)^{-1} \varepsilon_{nk}^0 - 2B\tau_\alpha^R x_{ij}^\alpha \gamma_{jk} \varepsilon_{kn}^0 \right). \end{aligned} \quad (11)$$

In the zero-th approximation for χ and ψ , variable $u_{ik}^\alpha = 0$ and Equations (6) and (8) take the form

$$\begin{aligned} \sigma_{ik} &= -p_0 \delta_{ik} + 3nT \sum_\alpha \left(x_{ik}^\alpha - \frac{1}{3} \delta_{ik} \right), \quad (12) \\ \frac{d}{dt} x_{ik}^\alpha - v_{ij} x_{jk}^\alpha - v_{kj} x_{ji}^\alpha \\ &= -\frac{1+(\kappa-\beta)a_{jj}}{B\tau_\alpha^R} \left(x_{ik}^\alpha - \frac{1}{3} \delta_{ik} \right) \\ & - \frac{3\beta}{2B\tau_\alpha^R} \left(\left(x_{ij}^\alpha - \frac{1}{3} \delta_{ij} \right) a_{jk} + \left(x_{kj}^\alpha - \frac{1}{3} \delta_{kj} \right) a_{ji} \right). \end{aligned}$$

The parameters of this system are $B\tau^*$, β , and κ . Note that when $N = 1$, system (12) is the system of equations for a dumbbell model

$$\begin{aligned} \sigma_{ik} &= -p_0 \delta_{ik} + 3 \frac{\eta_0}{\tau_0} a_{ik} \\ \frac{d}{dt} a_{ik} - v_{ij} a_{jk} - v_{kj} a_{ji} + \frac{1+(\kappa-\beta)I}{\tau_0} a_{ik}, \quad (13) \\ &= \frac{2}{3} \gamma_{ik} - \frac{3\beta}{\tau_0} a_{ij} a_{jk} \end{aligned}$$

where $\eta_0 = nT\tau_0$ and τ_0 are the initial shear viscosity and the relaxation time, and $I = a_{ii}$. The system (13) under the assumption of isotropic relaxation ($\beta = 0$), is followed by the well-known structural phenomenological Vinogradov-Pokrovskii model [13,14-17].

The model (13) is simple and gives high accuracy in describing steady nonlinear effects, though it is only the zero-order approximation model, which does not permit one to predict all features of polymer flow. In case, one needs more details, one can consider the contributions of parameters χ and ψ which take into account the relaxation character of the environment and the intrinsic viscosity in the equations for macromolecule dynamics.

4. Linear Effects of the Rheological Model

To obtain an expression for the dynamic shear modulus that corresponds to system (6), (8), and (9), we find a solution to this system in a linear approximation with respect to the velocity gradients. In this case, anisotropy

tensor a_{ik} is equal to zero, and the terms ω_{ik} can be omitted. Then (8) and (9) are written as

$$\begin{aligned} \tau_\alpha \frac{d}{dt} x_{ik}^\alpha + x_{ik}^\alpha &= \frac{1}{3} \delta_{ik} + \left(p \frac{\tau}{2} + B\tau_\alpha^R \right) (x_{ij}^\alpha \gamma_{jk} + x_{kj}^\alpha \gamma_{ji}), \\ \tau_\alpha^B \frac{d}{dt} u_{ik}^\alpha + u_{ik}^\alpha &= \psi \frac{\tau_\alpha^B}{\tau} \left(x_{ik}^\alpha - \frac{1}{3} \delta_{ik} - 2B\tau_\alpha^R x_{ij}^\alpha \gamma_{jk} \right) \\ & + \tau_\alpha^B (p u_{ij}^\alpha \gamma_{jk} + u_{kj}^\alpha \gamma_{ji}) \end{aligned}$$

where $\tau_\alpha = \tau/2 + (1+\psi)B\tau_\alpha^R$; $\tau_\alpha^B = 2\tau\tau_\alpha/(\tau + 2\tau_\alpha)$

The latter equations can be written as

$$\begin{aligned} x_{ik}^\alpha &= \frac{1}{3} \delta_{ik} \\ & + \frac{p\tau + 2B\tau_\alpha^R}{2\tau_\alpha} \int_0^\infty (x_{ij}^\alpha \gamma_{jk} + x_{kj}^\alpha \gamma_{ji}) \Big|_{t-s} \exp(-s/\tau_\alpha) ds \\ u_{ik}^\alpha &= \int_0^\infty \left(x_{ij}^\alpha \gamma_{jk} + x_{kj}^\alpha \gamma_{ji} + \frac{\psi}{\tau} \left(x_{ik}^\alpha - \frac{1}{3} \delta_{ik} - 2B\tau_\alpha^R x_{ij}^\alpha \gamma_{jk} \right) \right) \Big|_{t-s} \\ & \times \exp(-s/\tau_\alpha^B) ds \end{aligned} \quad (14)$$

Solving the first equation of (14) by the method of successive approximations with first-order approximation due to the velocity gradients, we obtain

$$x_{ik}^\alpha = \frac{1}{3} \delta_{ik} + \frac{p\tau + 2B\tau_\alpha^R}{3\tau_\alpha} \int_0^\infty \gamma_{ik}(t-s) \exp(-s/\tau_\alpha) ds.$$

Substitution of this expression into the second equation in (14) yields

$$\begin{aligned} u_{ik}^\alpha &= -\frac{2\psi}{3\tau} B\tau_\alpha^R \int_0^\infty \gamma_{ik}(t-s) \exp(-s/\tau_\alpha^B) ds \\ & + \psi \frac{p\tau + 2B\tau_\alpha^R}{3\tau_\alpha \tau} \int_0^\infty \int_0^\infty \gamma_{ik}(t-s-s') \exp(-s/\tau_\alpha) \\ & \cdot \exp(-s'/\tau_\alpha^B) ds ds'. \end{aligned}$$

In the simple oscillating shear flow $v_{12} \sim \exp(-i\omega t)$ and the last two expressions together with (6) define the complex shear modulus $G(\omega) = -i\omega\sigma_{12}(\omega, t)/v_{12}(\omega, t)$

$$\begin{aligned} 2 \frac{G(\omega)}{nT} &= \sum_\alpha \left(1 - \psi \frac{\tau_\alpha \tau_\alpha^B}{\tau(\tau_\alpha - \tau_\alpha^B)} \right) \frac{-i\omega(p\tau + 2B\tau_\alpha^R)}{1 - i\omega\tau_\alpha} \\ & + \psi \frac{(p\tau\tau_\alpha^B + 2B\tau_\alpha^R\tau_\alpha)}{\tau(\tau_\alpha - \tau_\alpha^B)} \frac{-i\omega\tau_\alpha^B}{1 - i\omega\tau_\alpha^B}. \end{aligned} \quad (15)$$

Next, it is convenient to distinguish the real and imaginary parts in $G(\omega)$: $G(\omega) = G'(\omega) - iG''(\omega)$.

If the value of the modulus on the plateau is determined by (15), then

$$G'_p(\omega) = \lim_{\omega \rightarrow \infty} G'(\omega) = nT \sum_{\alpha} \frac{(p\tau + 2B\tau_{\alpha}^R)(\tau + \psi B\tau_{\alpha}^R)}{\tau(\tau/2 + (1+\psi)B\tau_{\alpha}^R)} \quad (16)$$

This series converges only for $p = 0$. Thus, the Jaumann derivative in the equations of dynamics of a macromolecule (2) and (3) corresponds to cases *a*) and *b*). The definitions of the relaxation times τ , τ_{α}^R , and τ_{α} are given through parameters χ and ψ , estimates of which are given in [4,9], where it was shown that, for sufficiently long chains, one can always assume $\chi \ll 1$. As to intrinsic viscosity parameter ψ , here two alternative cases $\psi \ll 1$ and $\psi \gg 1$ are distinguished.

The curves of $G'(\omega^*)$ and $G''(\omega^*)$ versus the dimensionless frequency $\omega^* = B\tau^*\omega$ calculated by (18) are given in **Figures 1-4**, from which one can see that the values of $G'(\omega^*)$ and $G''(\omega^*)$ are mainly determined by parameter χ , and the impact of parameter ψ (for $\psi \ll 1$) is insignificant. The existence of characteristic plateau is determined by relaxation time τ . In the case, when $\tau = 0$, that corresponds to dilute solutions, irrespective of the type of convective derivative, a plateau on $G'(\omega^*)$ is absent. For $\psi \gg 1$, which corresponds to the dynamics of melts and strongly concentrated solutions [4], from (16) we have $G'_n = (\pi^2/12)nT\chi^{-1}$. The calculation results show that, for $\psi \ll 1$, the modulus on the plateau $G'_n \sim \chi^{-1/2}$.

Therefore, the non-dependence of G'_n on the molecular weight of a polymer means $\chi \sim M^{-2}$. Using the estimate for $\chi \sim c^{-2}M^{-1}$ obtained in [11], from the last relation one can obtain

$$G'_p \sim c^3 M^0.$$

The value of the initial shear viscosity η_0 , which can be expressed from (16) as

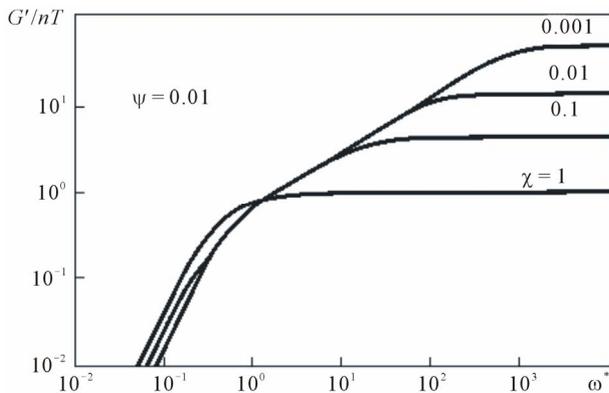


Figure 1. The contribution of parameter χ to the dimensionless frequency dependence of real component of dynamic modulus $G'(\omega^*)$.

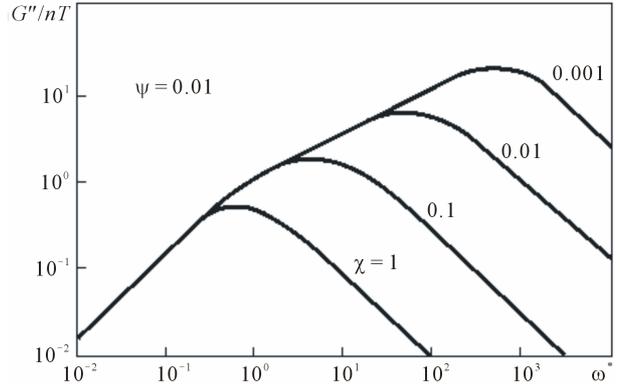


Figure 2. The contribution of parameter χ to the dimensionless frequency dependence of imaginary component of dynamic modulus $G''(\omega^*)$.

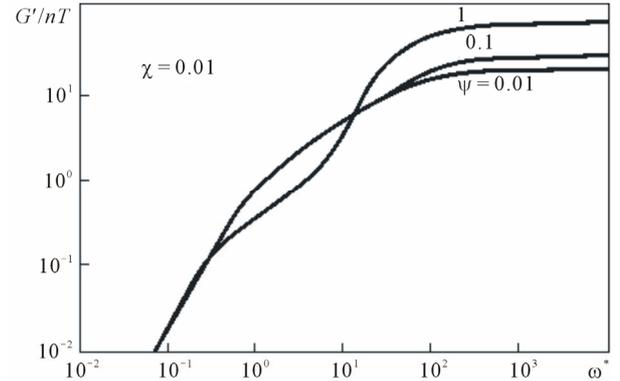


Figure 3. The contribution of parameter χ (internal viscosity) to the dimensionless frequency dependence of real component of dynamic modulus $G'(\omega^*)$.

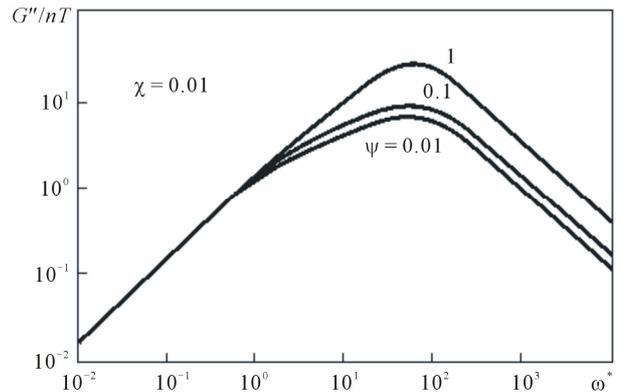


Figure 4. The contribution of parameter ψ (internal viscosity) to the dimensionless frequency dependence of imaginary component of dynamic modulus $G''(\omega^*)$.

$$\eta_0 = \lim_{\omega \rightarrow 0} \frac{G''(\omega)}{\omega} = \frac{\pi^2}{6} nT B\tau^* \quad (17)$$

To compare the calculation and experimental results,

we turn to the data of Menezes and Graessley [16,17], where $G'(\omega)$ and $G''(\omega)$ were measured for solutions of polybutadiene with different molecular weights at the same concentration of $c = 0.0676$ g/cm. The above formulae allow us to find the following estimates of the parameters of the rheological model (6), (8), and (9) were obtained: $\chi = 0.077; 0.025; 0.011$ and 0.005 , $B\tau^* = 0.21; 2.35; 16.27$ and 147 sec, and $nT = 840.4; 480.2; 321.5$ and 206.7 Pa for molecular weights

$M = 2 \times 10^5; 3.4 \times 10^5; 5.17 \times 10^5; 8.13 \times 10^5$, respectively. In all cases, $\psi = 0.025$. The comparison of the results is given in **Figures 5** and **6**, from which one can see satisfactory agreement between the theoretical and experimental curves of $G'(\omega)$ and $G''(\omega)$ for $\omega < 10$ sec⁻¹. The values of χ as a function of M are given on **Figure 7** showing good agreement with (17).

Figure 7 presents parameter χ dependence molecular weight corresponding $G'_p \sim \chi^{-1/2}$.

5. Non Linear Effects in the Simple Shear Flow

The system of constitutive Equations (6), (8), and (9) should be checked for correspondence to polymer fluid

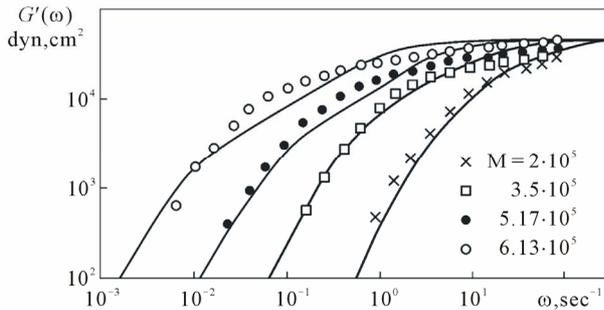


Figure 5. Real component of dynamic modulus $G'(\omega)$ for polybutadiene solutions of various molecular weights (points) [16,17], compared with the predictions of Equation (15) (solid lines).

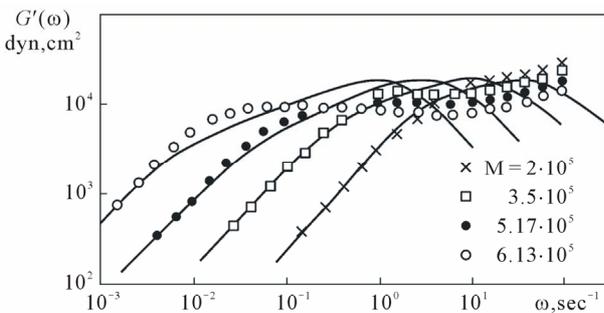


Figure 6. Imaginary component of dynamic modulus $G''(\omega)$ for polybutadiene solutions of various molecular weights (points) [16,17], compared with the predictions of Equation (15) (solid lines).

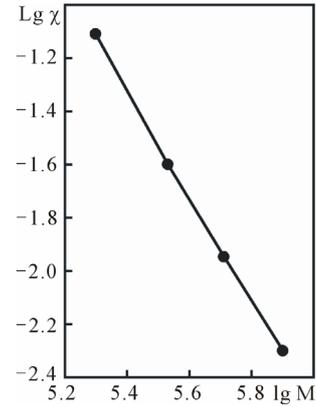


Figure 7. Parameter χ dependence on molecular weight.

flows. Diverse flows leads to difficult mathematical problems and, naturally, the check of the RES should be start 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 $v_{12}(t)$, which varies with time due to a well-known law. In steady flow, the gradient of velocity is constant, and rheological behavior of the polymer system is conveniently characterized by the following viscometric functions: shear viscosity η and first N_1 and second N_2 normal stresses differences, which are given by

$$\eta = \sigma_{12}/v_{12}, N_1 = \sigma_{11} - \sigma_{22}, N_2 = \sigma_{22} - \sigma_{33} \quad (18)$$

The dependence $v_{12}(t)$ is often given in the form $v_{12}(t) = \gamma E(t)$ or $v_{12}(t) = \gamma E(-t)$. Here γ is the shear velocity and $E(t)$ is the unit function of Heaviside. In the first case, system (6), (8), and (9) describes the establishment of stresses from the state of rest, and the corresponding viscometric functions (18) 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 are denoted by $\eta^-(\gamma, t)$ and $N_1^-(\gamma, t)$ and are generally functions of the velocity gradient and time. The following relations are apparently valid

$$\eta(\gamma) = \lim_{t \rightarrow \infty} \eta^+(\gamma, t), N_1 = \lim_{t \rightarrow \infty} N_1^+(\gamma, t). \quad (19)$$

Solving (8) for case of a simple shear flow with shear velocity v_{12} with third-order accuracy with respect to v_{12} , for viscometric functions we obtain

$$\psi_1 = \frac{\sigma_{11} - \sigma_{22}}{(v_{12})^2} = \frac{\pi^4}{45} nT,$$

$$\psi_2 = \frac{\sigma_{22} - \sigma_{33}}{(v_{12})^2} = -\frac{\pi^4}{90} \beta nT,$$

$$\eta = \frac{\sigma_{12}}{v_{12}} = \eta_0 \left[1 - \frac{4\pi^4}{105} \left(\frac{2}{5} \beta + \frac{\kappa - \beta}{9} \right) (B\tau^* v_{12})^2 \right].$$

Thus, the parameters κ and β are responsible for the nonlinear properties of system (12). For simple shear, β appears even in the second order with respect to the velocity gradients, and κ appears only in the third.

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

$$N_2 = -\left(\frac{15}{2\pi^2}\chi + \frac{1}{2}\beta\right)N_1, \quad (20)$$

obtained in [6]. Thus the model describes a non-zero second normal stress difference. The calculations show that, for $\psi \ll 1$, formula (20) remains valid for $\gamma B\tau^* < 10$.

To compare RES (6), (8), and (9) with experiments, we use the data of Menezes and Graessley [16,17], who studied shear flows of polybutadiene solutions with various molecular weights. It is convenient to use their results, because their data on linear viscoelasticity have already been compared with (6), (8), and (9) in Section 4.

The results of the calculation for the viscometric functions (18) and the corresponding experimental values are given in **Figures 8, 9** and **10**. In the calculations, we used the following induced anisotropy parameters: $\kappa = 0.1$, $\beta = 0.25$, $\varepsilon = 0$, 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 [16,17].

Let us consider nonlinear unsteady effects. The results of the calculation of the establishment of stresses for a

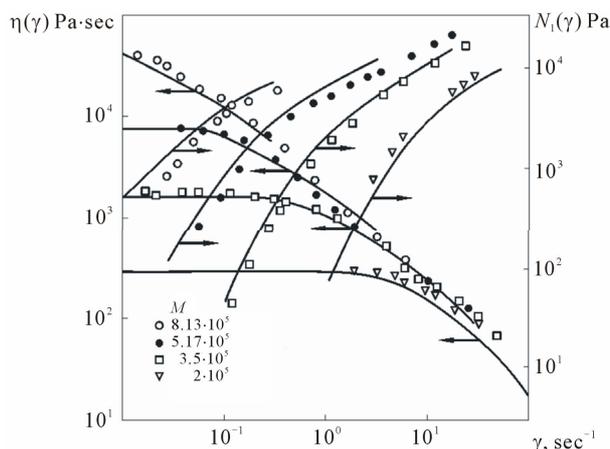


Figure 8. Experimental (solid lines) and theoretical (points) plots of the steady shear viscosity coefficient and the first difference of normal stresses vs. the shear velocity for various values of the molecular weight.

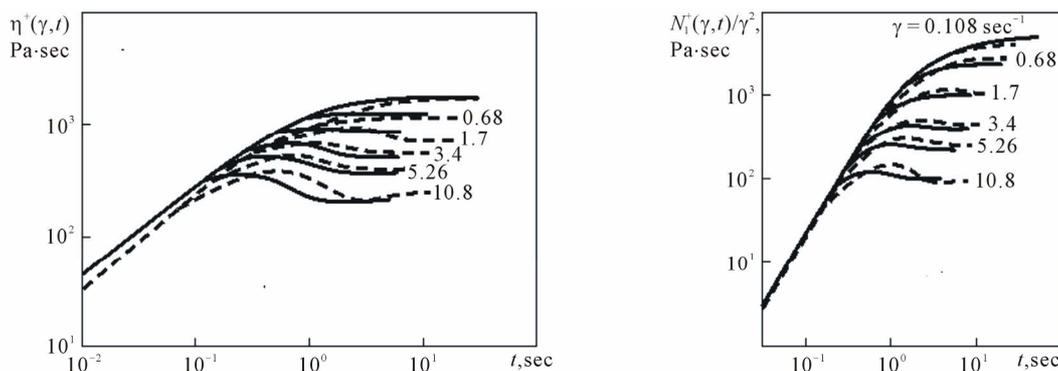


Figure 9. The comparison of experimental (solid lines) and theoretical (dashed lines) dependences of an establishment of stationary values of the shear viscosity coefficient and the first difference of normal stresses at various shear velocities.

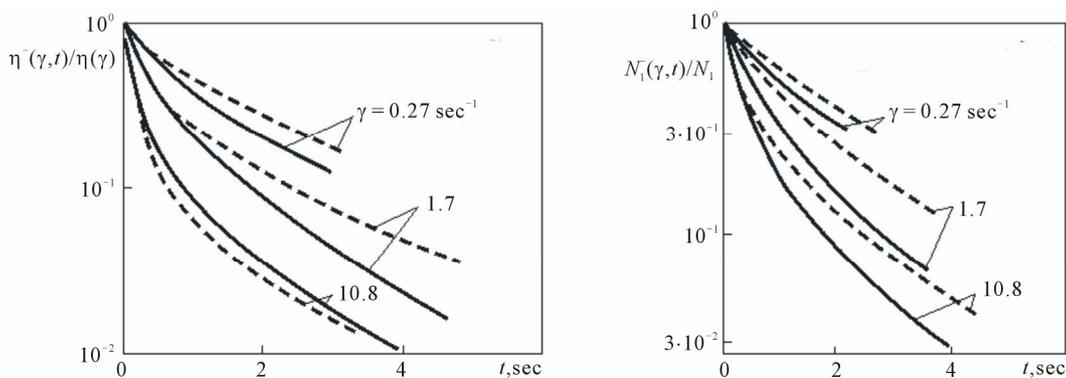


Figure 10. The comparison of experimental (solid lines) and theoretical (dashed lines) dependences of relaxation of the shear viscosity coefficient and the first difference of normal stresses after shear deformation at various shear velocities.

specimen with $M = 3.5 \times 10^5$ are given in **Figure 9**, which shows that Equations (2), (4), and (5) describes (the non-monotonic attainment of $\eta^+(\gamma, t)$ and $N_1^+(\gamma, t)$ at high shear velocities. It is also found that $\eta^+(\gamma, t) \sim t$ and $N_1^+(\gamma, t) \sim t^2$ at small t .

The data for $\eta^-(\gamma, t)$ and $N_1^-(\gamma, t)$ are given in **Figure 10**, which show that (18), (8) and (19) confirm the presence of two characteristic times for stress relaxation after intense shear deformation. The anisotropy parameter values are the same as in **Figures 8 and 9**.

6. Conclusion

Thus, the proposed microstructural approach to the description of the dynamics of polymer fluids does not contradict the available experimental data on the linear and non linear viscoelasticity of linear polymer solutions and melts. The obtained rheological equation of state is applicable for the description of steady and unsteady effects in both linear and nonlinear regions of strain rates and more complex flow regimes of linear polymer solutions and melts. The model can serve as a basis for the description of nonlinear effects in polymeric systems.

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Appendix: Derivation of Relaxation Equations

We introduce relaxation equations for the dimensionless moments x_{ik}^α and u_{ik}^α . In the inertia-free case ($m = 0$), Equations (1)-(4) can be written as

(A1)

Here

$$\xi_i^\alpha(t) = \frac{\tau}{4T\mu\lambda_\alpha} \left(\frac{d}{dt} \Phi_i^\alpha - (\omega_{ij} + p\gamma_{ij}) \Phi_j^\alpha + \frac{1}{\tau} \Phi_i^\alpha \right)$$

is a new random process which is δ correlated [9], $\tau_\alpha^R = \zeta / (4T\mu\lambda_\alpha) = \tau^* / \alpha^2$ is a set of the Rouse relaxation times, and $\psi = E/B$ is the measure of intrinsic viscosity.

Using (8), we obtain a closed system of equations for the moments $\langle \rho_i^\alpha \rho_k^\alpha \rangle$ and $\langle \rho_i^\alpha \psi_k^\alpha \rangle$:

$$\frac{d}{dt} \langle \rho_i^\alpha \rho_k^\alpha \rangle = \langle \rho_i^\alpha \psi_k^\alpha \rangle + \langle \rho_k^\alpha \psi_i^\alpha \rangle, \quad (A2)$$

$$\begin{aligned} & \left[\frac{\tau}{2} \delta_{kj} + B\tau_\alpha^R (\beta_{kj}^0 + \psi \varepsilon_{kj}^0) \right] \left[\langle \rho_i^\alpha \psi_j^\alpha \rangle - \omega_{jn} \langle \rho_i^\alpha \rho_n^\alpha \rangle \right] \\ &= -\frac{1}{2} \langle \rho_i^\alpha \rho_k^\alpha \rangle + \left(p \frac{\tau}{2} \delta_{ij} + B\tau_\alpha^R \beta_{ij}^0 \right) \gamma_{jn} \langle \rho_i^\alpha \rho_n^\alpha \rangle \langle \rho_i^\alpha \rho_k^\alpha \rangle \\ &+ \langle \rho_i^\alpha \xi_k^\alpha \rangle \end{aligned}$$

The moment $\langle \rho_i^\alpha \xi_k^\alpha \rangle$ which is unknown in (A2), can be found from the fluctuation-dissipation theorem. Besides there is another method. The equilibrium values of the moments $\langle \rho_i^\alpha \rho_k^\alpha \rangle$ and $\langle \rho_i^\alpha \psi_k^\alpha \rangle$ were determined previously by Pokrovskii [6]:

$$\langle \rho_i^\alpha \rho_k^\alpha \rangle_0 = \frac{1}{2\mu\lambda_\alpha} \delta_{ik}, \quad \langle \rho_i^\alpha \psi_k^\alpha \rangle_0 = 0 \quad (A3)$$

These values should be obtained from (A2) at zero velocity gradients, and the moments $\langle \rho_i^\alpha \rho_k^\alpha \rangle$ and $\langle \rho_i^\alpha \psi_k^\alpha \rangle$ enter into (A2) in a linear manner. Hence, taking into account the desired moment $\langle \rho_i^\alpha \xi_k^\alpha \rangle$, in (A2) we should replace the moments $\langle \rho_i^\alpha \rho_k^\alpha \rangle$ and $\langle \rho_i^\alpha \psi_k^\alpha \rangle$ that do not have the velocity-gradient tensor as a cofactor by $\langle \rho_i^\alpha \rho_k^\alpha \rangle - \langle \rho_i^\alpha \rho_k^\alpha \rangle_0$ and $\langle \rho_i^\alpha \psi_k^\alpha \rangle - \langle \rho_i^\alpha \psi_k^\alpha \rangle_0$, respectively.

Going over to the dimensionless moments x_{ik}^α in (9), we have

$$\begin{aligned} & \frac{D}{Dt} x_{ik}^\alpha - x_{ij}^\alpha \gamma_{jn} c_{nk}^\alpha - x_{kn}^\alpha \gamma_{jn} c_{ni}^\alpha \\ &= -\frac{1}{2B\tau_\alpha^R} \left(\left(x_{ik}^\alpha - \frac{1}{3} \delta_{ik} \right) b_{jk}^\alpha + \left(x_{kj}^\alpha - \frac{1}{3} \delta_{kj} \right) b_{ji}^\alpha \right), \quad (A4) \end{aligned}$$

where

$$b_{ik}^\alpha = \left(\frac{\tau}{2B\tau_\alpha^R} \delta_{ik} + \beta_{ik}^0 + \psi \varepsilon_{ik}^0 \right)^{-1};$$

$$c_{ik}^\alpha = \left(p \frac{\tau}{2B\tau_\alpha^R} \delta_{ij} + \beta_{ij}^0 \right) b_{jk}^\alpha;$$

$$\frac{D}{Dt} x_{ik}^\alpha = \frac{d}{dt} x_{ik}^\alpha - \omega_{ij} x_{jk}^\alpha - \omega_{kj} x_{ij}^\alpha$$

is the Jaumann derivative of the tensor quantity x_{ik}^α .

Multiplying (A1) by ρ_i^α and averaging the resulting expression, we write the following equation for u_{ik}^α :

$$\begin{aligned} & \tau \left(\frac{d}{dt} u_{ik}^\alpha - \omega_{kj} u_{ij}^\alpha - p \gamma_{kj} u_{ij}^\alpha \right) - \frac{\tau}{3T} \langle \psi_i^\alpha T_k^\alpha \rangle + u_{ik}^\alpha \\ &= -\frac{\zeta B \psi}{3T} \beta_{ij}^0 \left(\langle \rho_i^\alpha \psi_j^\alpha \rangle - \omega_{jn} \langle \rho_i^\alpha \rho_n^\alpha \rangle \right) \end{aligned} \quad (A5)$$

We find the moment $\langle \psi_i^\alpha T_k^\alpha \rangle$ entering into (A5) by multiplying (A1) by T_k^α and performing averaging. Using (A3), we finally obtain

$$\begin{aligned} & \frac{D}{Dt} u_{ik}^\alpha - p \gamma_{kj} u_{ij}^\alpha - c_{ij}^\alpha \gamma_{jn} u_{kn}^\alpha + \frac{1}{2B\tau_\alpha^R} c_{ij}^\alpha u_{jk}^\alpha + \frac{1}{\tau} u_{ik}^\alpha \\ &= \frac{\psi}{\tau} \left(\left(x_{ij}^\alpha - \frac{1}{3} \delta_{ij} \right) f_{jk}^\alpha - 2B\tau_\alpha^R x_{ij}^\alpha \gamma_{jn} d_{nk}^\alpha \right) \\ & \left(f_{ik}^\alpha = b_{ij}^\alpha \varepsilon_{kj}^0, \quad d_{ik}^\alpha = c_{ij}^\alpha \varepsilon_{kj}^0 \right). \end{aligned} \quad (A6)$$

Since the expression for the stress tensor (6) is written in symmetric form, it is more convenient to use the variable $y_{ik}^\alpha = (u_{ik}^\alpha + u_{ki}^\alpha) / 2$ instead of u_{ik}^α . The equation for this variable can be obtained from (9) using the symmetry of tensors c_{ik}^α and b_{ik}^α and assuming the permutability of tensors u_{ik}^α with γ_{ik} , c_{ik}^α , and b_{ik}^α . Assuming the existence 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. Then, instead of (9), one obtains

$$\begin{aligned} & \frac{D}{Dt} y_{ik}^\alpha - \frac{1}{2} \left(c_{ij}^\alpha \gamma_{jn} y_{kn}^\alpha + c_{kj}^\alpha \gamma_{jn} y_{ni}^\alpha \right) \\ &+ \frac{1}{4B\tau_\alpha^R} \left(b_{ij}^\alpha y_{jk}^\alpha + b_{kj}^\alpha y_{ji}^\alpha \right) + \frac{1}{\tau} y_{ik}^\alpha \\ &= \frac{\psi}{2\tau} \left(\left(x_{ij}^\alpha - \frac{1}{3} \delta_{ij} \right) f_{jk}^\alpha - 2B\tau_\alpha^R x_{ij}^\alpha \gamma_{jn} d_{nk}^\alpha \right) \\ &+ \frac{\psi}{2\tau} \left(\left(x_{kj}^\alpha - \frac{1}{3} \delta_{kj} \right) f_{ji}^\alpha - 2B\tau_\alpha^R x_{kj}^\alpha \gamma_{jn} d_{ni}^\alpha \right). \end{aligned} \quad (A7)$$