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STRUCTURAL-KINETIC APPROACH IN THE THEORY OF FLOWS OF LINEAR-POLYMER SOLUTIONS AND MELTS

G. V. Pyshnograi

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The formulation of a rheological equation of state (RES) that establishes a relationship between the stress tensor, kinetic characteristics, and internal thermodynamic parameters is the main problem of the dynamics of linear-polymers solutions and melts. At present, a large number of such equations of various complexity [1, 2] are known, but a consistent theory of linear and nonlinear relaxation phenomena in polymer systems has not yet been developed. This is due to both the complex topology of these systems, which are formed by tangled macromolecules, and mathematical difficulties [3].

Phenomenological and microstructural approaches are used in writing RES. The RES obtained phenomenologically are a certain interpolation of experimental data. To describe different types of flows within the framework of a single model, RES are obtained in the most general form [2]. In this case, application of RES to an actual polymer system can become an insoluble problem.

In the microstructural approach, methods of statistical mechanics are used. However, to obtain closed systems of equations, often one has to introduce additional assumptions, In turn, this sometimes involves insuperable difficulties in attempts to generalize one or another theory. At the same time, an advantage of the microstructural approach is the possibility of studying the relationship between the microcharacteristics of a polymer system (concentration and molecular weight of the polymer) and macroscopically observed quantities (viscosity, shear and normal stresses, etc.). In this connection, it is of interest, using microstructural concepts, to formulate a sequence of RES that takes into account new molecular effects in each step. Pyshnograi et al. [4–6] 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 [4–6] 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. The resulting equations can be recommended as a first approximation in constructing a sequence of RES.

Dynamics of a Macromolecule in Flow. The microstructural approach to the description of the dynamics of polymer systems is based on model concepts of motion of polymer systems. Realization of this approach involves sequential solution of two problems: formulation of the equations of dynamics for a macromolecule and transition from the formulated equations to RES. Since it is difficult to take into account the details of the chemical structure of polymers, the equations of dynamics of the macromolecule cannot be formulated without additional assumptions. Two significant assumptions are used most often:

(1) A monomolecular approximation in which a single chosen molecule moving in the effective medium formed by the solvent and the other molecules is considered instead of the entire set of macromolecules in the volume.

(2) The possibility of identifying, irrespective of the chemical nature of the polymer, the slow thermal motions of the chosen macromolecule with the motion of N centers of friction (beads) connected in series by elastic entropy forces (springs). These assumptions lead to the following equations of the dynamics of macromolecules [5–8]:

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

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where ρ_i^α and ψ_i^α are the ith components of 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 intrinsic viscous force, Φ_i^α is a random force, and $2T\mu\lambda_\alpha$ is the coefficient of elasticity.

The definition of the 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. The force Γ_i^α describes the interaction of the polymer chain with the environment via the solvent. For dilute polymer systems, in which polymer macromolecules can be considered noninteracting, the force Γ_i^α can be found by solving the problem of particle motion in a viscous fluid in the Stokes approximation:

$$\Gamma_i^\alpha = -\zeta(\psi_i^\alpha - \nu_{ij}\rho_j^\alpha). \tag{2}$$

Here ζ is the friction coefficient of a bead in a monomer fluid, ν_{ij} is the velocity-gradient tensor, which is conveniently expressed below as the sum of symmetric γ_{ij} and antisymmetric 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. Expression (2) is the basis for the description of the dynamics of dilute polymer systems [8].

In modeling of concentrated polymer systems, in which macromolecules cannot be considered noninteracting, expression (2) needs generalization. This is caused by the necessity of taking 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 side of the monomer solvent, but also from the side of other macromolecules. Furthermore, one should take into account that, in a flow with nonzero velocity gradients, a macromolecular coil elongates along the flow, and the medium formed by the elongated coils becomes anisotropic. This anisotropy of the mobility of beads is called induced and is determined by the shape and orientation of macromolecular coils [9, 10]. Allowance for all these factors leads to the following equation for the force of hydrodynamic entrainment:

$$\tau\left(\frac{d}{dt}\Gamma_i^\alpha - \omega_{ij}\Gamma_j^\alpha - p\gamma_{ij}\Gamma_j^\alpha\right) + \Gamma_i^\alpha = -\zeta B\beta_{ij}^0(\psi_j^\alpha - \nu_{jn}\rho_n^\alpha). \tag{3}$$

Here τ is the relaxation time of the environment, β_{ij}^0 is the dimensionless tensor friction coefficient of a bead, B is the measure of strengthening of the friction coefficient ζ, and p is a parameter.

The bracketed expression on the left side of (3) is a substantial derivative of the vector quantity Γ_i^α [1]. The presence of this derivative allows one to satisfy the principle of material objectivity in Eq. (3) [1, 2]. The 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, and, 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 (3) is determined below.

When macromolecules form a tangled system, in addition to the force of hydrodynamic entrainment, one should take into account the intrinsic viscous force Γ_i^α, as is shown by Pokrovskii [7, 8]. The specific requirement imposed on the force T_i^α is the vanishing of this force with rotation of a macromolecular coil as a unit [7, 8]. This allows one to replace (2) by the expression

$$T_i^\alpha \sim (\psi_i^\alpha - \omega_{ij}\rho_j^\alpha).$$

The intrinsic viscous force T_i^α, like Γ_i^α, is of a relaxation character and depends on the anisotropic properties of the environment. Therefore, the first expression for this force can be written in a similar manner as Eq. (3) in the form

$$\tau\left(\frac{d}{dt}T_i^\alpha - \omega_{ij}T_j^\alpha - p\gamma_{ij}T_j^\alpha\right) + T_i^\alpha = -\zeta E\varepsilon_{ij}^0(\psi_j^\alpha - \omega_{jn}\rho_n^\alpha), \tag{4}$$

where ε_{ij}^0 is the dimensionless tensor friction coefficient and E is the measure of strengthening of the friction coefficient ζ for the intrinsic viscous force T_i^α.

We assume that the anisotropy of mobility in the polymer system considered is characterized by the second-order symmetric tensor a_{ik}. Then, for the coefficients β^0_{ij} and ε^0_{ij} we write [9, 10]

$$\beta^0_{ik} = \left(\delta_{ik} + 3\beta\left(a_{ik} - \frac{a_{jj}}{3}\,\delta_{ik}\right) + æ a_{jj}\delta_{ik}\right)^{-1}, \quad \varepsilon^0_{ik} = \left(\delta_{ik} + 3\varepsilon\left(a_{ik} - \frac{a_{jj}}{3}\,\delta_{ik}\right) + \nu a_{jj}\delta_{ik}\right)^{-1}. \tag{5}$$

Thus, (1), (3)–(5) is the system of equations of dynamics of a macromolecule. The random force $\Phi^\alpha_i(t)$ entering into (1) is the Gaussian random process with a zero average. Its correlation tensor satisfies the corresponding fluctuation–dissipation relation in [7, 10].

Stress Tensor and Rheological Equation of State. The behavior of a polymer system based on Eqs. (1), (3), and (4) is discrete or microscopic. Transition to the continuous case, i.e., to the description of polymer-system flows within the framework of continuum mechanics, requires introduction of macroscopic variables — the density $\rho(\mathbf{x}, t)$ and the pulse density $\rho\boldsymbol{\nu}(\mathbf{x}, t)$. These variables are introduced in the standard manner [7, 8]:

$$\rho(\mathbf{x}, t) = \sum m\langle\delta(\mathbf{x} - \mathbf{r}^\alpha)\rangle, \quad \rho\boldsymbol{\nu}(\mathbf{x}, t) = \sum m\langle\mathbf{u}^\alpha\delta(\mathbf{x} - \mathbf{r}^\alpha)\rangle. \tag{6}$$

Here $\mathbf{r}^\alpha$ and $\mathbf{u}^\alpha$ are the radius vector and the velocity vector of a bead with number α, $\mathbf{x}$ is the radius vector of the chosen point in space, and t is time; summation is performed over all beads in a unit volume, and averaging is performed over the ensemble of all possible realizations of the random force $\Phi^\alpha_i(t)$.

Differentiating (6) with respect to time yields an equation of conservation of mass, and transformation to generalized coordinates with allowance for (1) yields an equation for pulse density. In the latter case, we have an expression for the stress tensor of a polymer system in terms of statistical characteristics of the solutions of system (1), (3), and (4):

$$\sigma_{ik} = -p_0\delta_{ik} + 3nT\sum_\alpha\left[x^\alpha_{ik} - \frac{1}{3}\,\delta_{ik} - \frac{1}{2}\,(u^\alpha_{ik} + u^\alpha_{ki})\right], \tag{7}$$

where p_0 is the pressure, n is the number of macromolecules in a unit volume, T is the temperature in energy units, and $x^\alpha_{ik} = 2\mu\lambda_\alpha\langle\rho^\alpha_i\rho^\alpha_k\rangle/3$ and $u^\alpha_{ik} = \langle\rho^\alpha_i T^\alpha_k\rangle/(3T)$ are internal thermodynamic parameters that describe the departure of a macroscopically nonequilibrium system from the state of equilibrium [11].

The thermodynamic variables x^α_{ik} entering into (7) characterize the inertial properties of a macromolecular coil and, hence, can be used to determine the anisotropy tensor a_{ik} in (5). Following [10], we write

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

Hence, it becomes possible to establish the physical meaning of the microanisotropy parameters entering into (5). These parameters take into account the dimensions $(æ, \nu)$ and shape (β, ε) of a macromolecular coil in the equations of dynamics of a macromolecule.

We introduce relaxation equations for the dimensionless moments x^α_{ik} and u^α_{ik}. In the inertia-free case $(m = 0)$, Eqs. (1), (3), and (4) can be written as

$$\left[\frac{\tau}{2}\,\delta_{ij} + B\tau^R_\alpha(\beta^0_{ij} + \psi\varepsilon^0_{ij})\right][\psi^\alpha_j - \omega_{jn}\rho^\alpha_n] = \left(p\,\frac{\tau}{2}\,\gamma_{ij} + B\tau^R_\alpha\beta^0_{in}\gamma_{nj} - \frac{1}{2}\,\delta_{ij}\right)\rho^\alpha_j + \xi^\alpha_i(t). \tag{8}$$

Here

$$\xi^\alpha_i(t) = \frac{\tau}{4T\mu\lambda_\alpha}\left(\frac{d}{dt}\,\Phi^\alpha_i - (\omega_{ij} + p\gamma_{ij})\,\Phi^\alpha_j + \frac{1}{\tau}\,\Phi^\alpha_i\right)$$

is a new random process which is δ correlated [10], $\tau^R_\alpha = \zeta/(4T\mu\lambda_\alpha) = \tau^*/\alpha^2$ 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 $\langle\rho^\alpha_i\rho^\alpha_k\rangle$ and $\langle\rho^\alpha_i\psi^\alpha_k\rangle$:

$$\frac{d}{dt}\,\langle\rho^\alpha_i\rho^\alpha_k\rangle = \langle\rho^\alpha_i\psi^\alpha_k\rangle + \langle\rho^\alpha_k\psi^\alpha_i\rangle,$$

$$\left[\frac{\tau}{2}\delta_{kj}+B\tau_{\alpha}^{R}(\beta_{kj}^{0}+\psi\varepsilon_{kj}^{0})\right]\left[\langle\rho_i^{\alpha}\psi_j^{\alpha}\rangle-\omega_{jn}\langle\rho_i^{\alpha}\rho_n^{\alpha}\rangle\right]=-\frac{1}{2}\langle\rho_i^{\alpha}\rho_k^{\alpha}\rangle+\left(p\frac{\tau}{2}\,\delta_{kj}+B\tau_{\alpha}^{R}\beta_{kj}^{0}\right)\gamma_{jn}\langle\rho_i^{\alpha}\rho_n^{\alpha}\rangle+\langle\rho_i^{\alpha}\xi_k^{\alpha}\rangle. \tag{9}$$

The moment $\langle\rho_i^{\alpha}\xi_k^{\alpha}\rangle$, which is unknown in (9), can be found from the fluctuation-dissipation theorem. But 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 [11]:

$$\langle\rho_i^{\alpha}\rho_k^{\alpha}\rangle_0=\frac{1}{2\mu\lambda_{\alpha}}\,\delta_{ik},\qquad\langle\rho_i^{\alpha}\psi_k^{\alpha}\rangle_0=0. \tag{10}$$

These values should be obtained from (9) 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 (9) in a linear manner. Hence, taking into account the desired moment $\langle\rho_i^{\alpha}\xi_k^{\alpha}\rangle$, in (9) 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

$$\frac{D}{Dt}\,x_{ik}^{\alpha}-x_{ij}^{\alpha}\gamma_{jn}c_{nk}^{\alpha}-x_{kn}^{\alpha}\gamma_{jn}c_{ni}^{\alpha}=-\frac{1}{2B\tau_{\alpha}^{R}}\left(\left(x_{ik}^{\alpha}-\frac{1}{3}\,\delta_{ik}\right)b_{jk}^{\alpha}+\left(x_{kj}^{\alpha}-\frac{1}{3}\,\delta_{kj}\right)b_{ji}^{\alpha}\right), \tag{11}$$

where

$$b_{ik}^{\alpha}=\left(\frac{\tau}{2B\tau_{\alpha}^{R}}\,\delta_{ik}+\beta_{ik}^{0}+\psi\varepsilon_{ik}^{0}\right)^{-1};\quad c_{ik}^{\alpha}=\left(p\,\frac{\tau}{2B\tau_{\alpha}^{R}}\,\delta_{ij}+\beta_{ij}^{0}\right)b_{jk}^{\alpha};\quad\frac{D}{Dt}\,x_{ik}^{\alpha}=\frac{d}{dt}\,x_{ik}^{\alpha}-\omega_{ij}x_{jk}^{\alpha}-\omega_{kj}x_{ij}^{\alpha}$$

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

Multiplying (4) by ρ_i^{α} and averaging the resulting expression, we write the following equation for u_{ik}^{α}:

$$\tau\left(\frac{d}{dt}\,u_{ik}^{\alpha}-\omega_{kj}u_{ij}^{\alpha}-p\gamma_{kj}u_{ij}^{\alpha}\right)-\frac{\tau}{3T}\,\langle\psi_i^{\alpha}T_k^{\alpha}\rangle+u_{ik}^{\alpha}=-\frac{\zeta B\psi}{3T}\,\beta_{ij}^{0}\left(\langle\rho_i^{\alpha}\psi_j^{\alpha}\rangle-\omega_{jn}\langle\rho_i^{\alpha}\rho_n^{\alpha}\rangle\right). \tag{12}$$

We find the moment $\langle\psi_i^{\alpha}T_k^{\alpha}\rangle$ entering into (12) by multiplying (8) by T_k^{α} and performing averaging. Using (10), we finally obtain

$$\begin{aligned}&\frac{D}{Dt}\,u_{ik}^{\alpha}-p\gamma_{kj}u_{ij}^{\alpha}-c_{iji}^{\alpha}\gamma_{jn}u_{kn}^{\alpha}+\frac{1}{2B\tau_{\alpha}^{R}}\,c_{ij}^{\alpha}u_{jk}^{\alpha}+\frac{1}{\tau}\,u_{ik}^{\alpha}\\&=\frac{\psi}{\tau}\left(\left(x_{ij}^{\alpha}-\frac{1}{3}\,\delta_{ij}\right)f_{jk}^{\alpha}-2B\tau_{\alpha}^{R}x_{ij}^{\alpha}\gamma_{jn}d_{n}^{\alpha}\right)\qquad(f_{ik}^{\alpha}=b_{ij}^{\alpha}\varepsilon_{kj}^{0},\quad d_{ik}^{\alpha}=c_{ij}^{\alpha}\varepsilon_{kj}^{0}).\end{aligned} \tag{13}$$

The RES (7), (11), and (13) define a nonlinear, anisotropic, viscoelastic fluid. These equations for $p=0$ coincide with those obtained in [9], where the Jaumann derivative was used in expressions (3) and (4) for the forces Γ_i^{α} and T_i^{α}. The behavior of system (7), (11), and (13) is determined by the six dimensionless parameters ($\chi=\tau/2B\tau^{*}$, ψ, β, ε, æ, and ν) and the two dimensional parameters ($B\tau^{*}$ and nT). The parameter χ characterizing the ratio of the relaxation time of the environment τ to the maximum relaxation time $B\tau^{*}$ was estimated in [7–10, 12], where it was shown that $\chi\ll1$ for sufficiently long polymer chains. As to the parameter ψ, here two cases can be distinguished: $\psi\ll1$ [4–8, 10] and $\psi\gg1$ [7, 12], which are discussed below. As in [10], it is convenient to consider simpler forms of these equations by using the smallness of the parameters χ and ψ.

Zeroth-Order Approximation Models. In the zeroth approximation for χ and ψ, the variable $u_{ik}^{\alpha}=0$ and Eqs. (7) and (11) take the form

$$\begin{gathered}\sigma_{ik}=-p_0\delta_{ik}+3nT\sum_{\alpha}\left(x_{ik}^{\alpha}-\frac{1}{3}\,\delta_{ik}\right),\\\frac{d}{dt}\,x_{ik}^{\alpha}-\nu_{ij}x_{jk}^{\alpha}-\nu_{kj}x_{ji}^{\alpha}=-\frac{1+(\text{æ}-\beta)a_{ss}}{B\tau_{\alpha}^{R}}\left(x_{ik}^{\alpha}-\frac{1}{3}\,\delta_{ik}\right)-\frac{3\beta}{2B\tau_{\alpha}^{R}}\left(\left(x_{ij}^{\alpha}-\frac{1}{3}\,\delta_{ij}\right)a_{jk}+\left(x_{kj}^{\alpha}-\frac{1}{3}\,\delta_{kj}\right)a_{ji}\right).\end{gathered} \tag{14}$$

The parameters of this system are $B\tau^{*}$, β, and æ. Solving Eqs. (14) for a simple shear flow with shear velocity ν_{12} with third-order accuracy with respect to ν_{12}, for viscosimetric functions we obtain

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

Thus, the parameters æ and β are responsible for the nonlinear properties of system (14). For simple shear, β appears even in the second order with respect to the velocity gradients, and æ appears only in the third.

In the case of a damb-bell model ($N = 1$), system (14) takes the form

$$\sigma_{ik} = -p_0 \delta_{ik} + 3\,\frac{\eta_0}{\tau_0}\, a_{ik}, \quad \frac{d}{dt}\, a_{ik} - \nu_{ij} a_{jk} - \nu_{kj} a_{ji} + \frac{1 + (æ - \beta) I}{\tau_0}\, a_{ik} = \frac{2}{3}\,\gamma_{ik} - \frac{3\beta}{\tau_0}\, a_{ij} a_{jk}, \tag{15}$$

where $\eta_0 = nT\tau_0$ and τ_0 are the initial shear viscosity and the relaxation time, and $I = a_{jj}$. Hence, under the assumption of isotropic relaxation ($\beta = 0$), we obtain the well-known structural phenomenological Pokrovskii's model [13].

Model (15) is considered in detail in [4-6], where good agreement between the model and the steady flows of solutions and melts of linear polymers of various molecular weights and concentrations with simple shear [6] and initial tension [4] was established.

First-Order Approximation Model. Aside from the advantages of the zeroth-order approximation model (15) (simplicity and high accuracy in describing steady nonlinear effects), the first-order approximation model does not permit one to predict all features of polymer flow. In particular, this is true for the dynamic modulus of shear. In this case, it is necessary to consider the contributions of the parameters χ and ψ, which take into account the relaxation character of the environment and the intrinsic viscosity in the equations of dynamics of a macromolecule.

Since only effects of the first order with respect to χ and ψ are of interest to us, we note that Eqs. (7) and (11) do not change, and Eq. (13) takes the form

$$\frac{D}{Dt} u^{\alpha}_{ik} - p\gamma_{kj} u^{\alpha}_{ij} - \gamma_{ij} u^{\alpha}_{jk} + \frac{1}{2B\tau^R_{\alpha}} (\beta^0_{ij})^{-1} u^{\alpha}_{jk} + \frac{1}{\tau} u^{\alpha}_{ik} = \frac{\psi}{\tau}\Big(\Big(x^{\alpha}_{ij} - \frac{1}{3}\,\delta_{ij}\Big)(\beta^0_{jn})^{-1} \varepsilon^0_{kn} - 2B\tau^R_{\alpha} x^{\alpha}_{ij} \gamma_{jn} \varepsilon^0_{nk}\Big). \tag{16}$$

To obtain an expression for the dynamic shear modulus that corresponds to system (7), (11), and (16), we find a solution of this system in a linear approximation with respect to the velocity gradients. In this case, the anisotropy tensor a_{ik} is equal to zero, and the terms ω_{ik} can be omitted. Then, Eqs. (11) and (16) are written as

$$\tau_{\alpha}\,\frac{d}{dt}\, x^{\alpha}_{ik} + x^{\alpha}_{ik} = \frac{1}{3}\,\delta_{ik} + \Big(p\,\frac{\tau}{2} + B\tau^R_{\alpha}\Big)(x^{\alpha}_{ij}\gamma_{jk} + x^{\alpha}_{kj}\gamma_{ji}),$$

$$\tau^B_{\alpha}\,\frac{d}{dt}\, u^{\alpha}_{ik} + u^{\alpha}_{ik} = \psi\,\frac{\tau^B_{\alpha}}{\tau}\Big(x^{\alpha}_{ik} - \frac{1}{3}\,\delta_{ik} - 2B\tau^R_{\alpha} x^{\alpha}_{ij}\gamma_{jk}\Big) + \tau^B_{\alpha}(p u^{\alpha}_{ij}\gamma_{jk} + u^{\alpha}_{kj}\gamma_{ji})$$

$$[\tau_{\alpha} = \tau/2 + (1 + \psi) B\tau^B_{\alpha}, \quad \tau^B_{\alpha} = 2\tau\tau_{\alpha}/(\tau + 2\tau_{\alpha})].$$

The latter equations can be written as

$$\begin{gathered} x^{\alpha}_{ik} = \frac{1}{3}\,\delta_{ik} + \frac{p\tau + 2B\tau^R_{\alpha}}{2\tau_{\alpha}} \int\limits_0^{\infty} (x^{\alpha}_{ij}\gamma_{jk} + x^{\alpha}_{kj}\gamma_{ji})\Big|_{t-s} \exp\left(-s/\tau_{\alpha}\right) ds, \\ u^{\alpha}_{ik} = \int\limits_0^{\infty} \Big[x^{\alpha}_{ij}\gamma_{jk} + x^{\alpha}_{kj}\gamma_{ji} + \frac{\psi}{\tau}\Big(x^{\alpha}_{ik} - \frac{1}{3}\,\delta_{ik} - 2B\tau^R_{\alpha} x^{\alpha}_{ij}\gamma_{jk}\Big)\Big]\Big|_{t-s} \exp\left(-s/\tau^B_{\alpha}\right) ds. \end{gathered} \tag{17}$$

Solving the first of Eqs. (17) by the method of successive approximations with first-order accuracy with respect to the velocity gradients, we obtain

$$x^{\alpha}_{ik} = \frac{1}{3}\,\delta_{ik} + \frac{p\tau + 2B\tau^R_{\alpha}}{3\tau_{\alpha}} \int\limits_0^{\infty} \gamma_{ik}(t - s) \exp\left(-s/\tau_{\alpha}\right) ds.$$

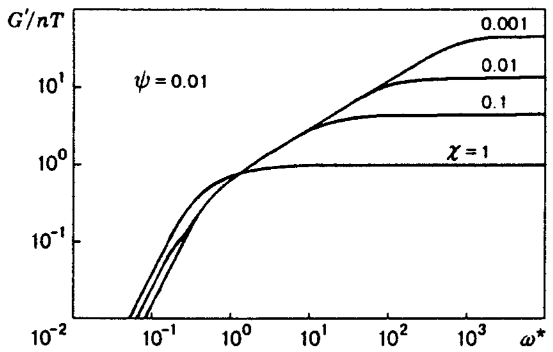

Fig. 1

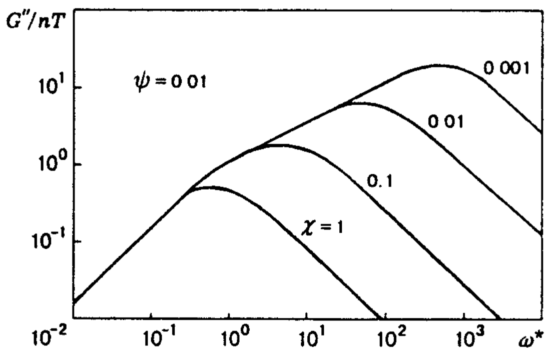

Fig. 2

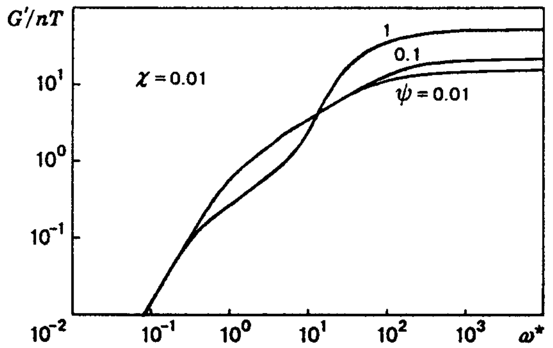

Fig. 3

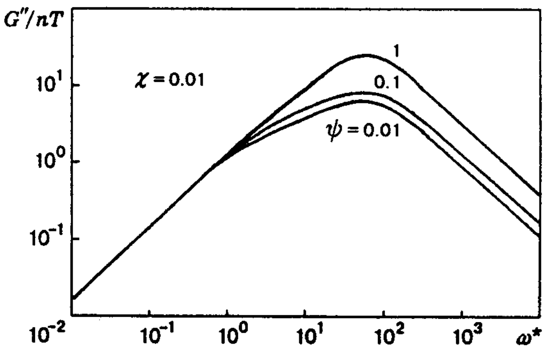

Fig. 4

Substitution of this expression into the second equation in (17) yields

$$u_{ik}^{\alpha} = -\frac{2\psi}{3\tau} B\tau_{\alpha}^{R} \int_{0}^{\infty} \gamma_{ik}(t-s)\exp(-s/\tau_{\alpha}^{B}), ds + \psi\,\frac{p\tau + 2B\tau_{\alpha}^{R}}{3\tau_{\alpha}\tau} \int_{0}^{\infty}\int_{0}^{\infty} \gamma_{ik}(t-s-s')\exp(-s/\tau_{\alpha})\exp(-s'/\tau_{\alpha}^{B})\, ds ds'.$$

For simple oscillating shear flow, for which $\nu_{12} \sim \exp(-i\omega t)$, the last two expressions together with (7) define the complex shear modulus $G(\omega) = -i\omega\sigma_{12}(\omega, t)/\nu_{12}(\omega, t)$

$$2\,\frac{G(\omega)}{nT} = \sum_{\alpha} \left(1 - \psi\,\frac{\tau_{\alpha}}{\tau(\tau_{\alpha} - \tau_{\alpha}^{B})}\right) \frac{-i\omega(\tau + 2B\tau_{\alpha}^{R})}{1 - i\omega\tau_{\alpha}} + \psi\,\frac{(\tau\tau_{\alpha}^{B} + 2B\tau_{\alpha}^{R}\tau_{\alpha})}{\tau(\tau_{\alpha} - \tau_{\alpha}^{B})}\,\frac{-i\omega\tau_{\alpha}^{B}}{1 - i\omega\tau_{\alpha}^{B}}. \tag{18}$$

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

When using expressions (18), one should distinguish three cases:

(a) highly concentrated ($c > 10\%$) solutions and melts of polymers,

(b) half-dilute polymer solutions over a wide range of strain rates ($c \sim$ 1–10%), and

(c) extremely dilute solutions ($c < 1\%$).

In the first two cases, the curves $G'(\omega)$ show a typical plateau, whose position depends weakly on the molecular weight of the polymer [14, 15], and in the third case, such a plateau is absent [14]. If the value of the modulus on the plateau is determined from (18), then

$$G_p'(\omega) = \lim_{\omega\to\infty} G'(\omega) = nT \sum_{\alpha} \frac{(p\tau + 2B\tau_{\alpha}^{R})(\tau + \psi B\tau_{\alpha}^{R})}{\tau(\tau/2 + (1+\psi)B\tau_{\alpha}^{R})}. \tag{19}$$

This series converges only for $p = 0$. Thus, to cases a and b corresponds the Jaumann derivative in the equations of dynamics of a macromolecule (3) and (4).

For extremely dilute solutions, usually, $\tau = 0$ [8]. In this case, irrespective of the type of convective derivative, a plateau on $G'(\omega)$ is absent.

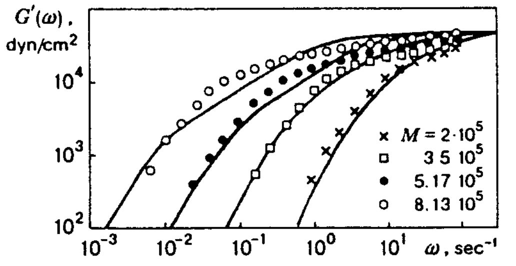

Fig. 5

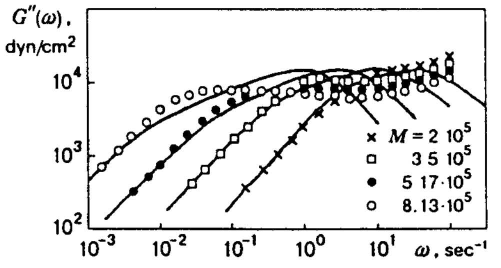

Fig. 6

We revert to the above estimates of the parameters χ and ψ entering into the definitions of the relaxation times τ, τ_α^R, and τ_α. These estimates are given in [7–10, 12], where it was shown that, for sufficiently long chains, one can always assume that $\chi \ll 1$. As to the intrinsic-viscosity parameter ψ, here two alternative cases $\psi \ll 1$ and $\psi \gg 1$ are distinguished. For $\psi \gg 1$, which corresponds to the dynamics of melts and strongly concentrated solutions, from (19) we have $G'_p = (\pi^2/12)nT\chi^{-1}$.

Using the estimate for $\chi \sim c^{-2}M^{-1}$ obtained by Pokrovskii and Pyshnograi [12], from the last relation one can obtain $G'_p \sim c^3M^0$, and this agrees well with the experimental data of Graessley [14]. A detaild review of papers studying the case of $\psi \gg 1$ is given by Pokrovskii [7]. We consider in more detail the case $\psi \ll 1$, which corresponds to the dynamics of polymer solutions with a concentration of the order of 1%. The curves of $G'(\omega)$ and $G''(\omega)$ versus the dimensionless frequency $\omega^* = B\tau^*\omega$ calculated by (18) are given in Figs. 1–4, from which one can see that the values of $G'(\omega)$ and $G''(\omega)$ are mainly determined by the parameter χ, and the effect of the parameter ψ (for $\psi \ll 1$) is insignificant. The calculation results show that, for $\psi \ll 1$, the modulus on the plateau $G'_p \sim \chi^{-1/2}$. Therefore, from the condition of nondependence of G'_p on the molecular weight of a polymer we have

$$\chi \sim M^{-2}. \tag{20}$$

To compare the calculation and experimental results, we turn to [15], where $G'(\omega)$ and $G''(\omega)$ were measured for solutions of polybutadiene with different molecular weights at the same concentration $c = 0.0676$ g/cm. In this case, the parameter $B\tau^*$ was estimated from the value of the initial shear viscosity η_0, which can be expressed from (19) as

$$\eta_0 = \lim_{\omega\to0} \frac{G''(\omega)}{\omega} = \frac{\pi^2}{6} nTB\tau^*.$$

The parameter $\chi = 0.025$ was chosen for $M = 3.5\cdot10^5$, and, for the other values of M, it was calculated using (20). A comparison of (18) and the data of [15] is given in Figs. 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}.

Thus, the proposed microstructural approach to the description of the dynamics of polymer fluids does not contradict the available experimental data on the linear viscoelasticity of linear-polymer solutions and melts and can serve as a basis for the description of nonlinear effects in these systems.

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