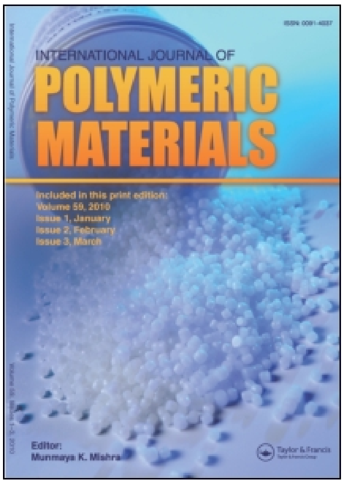

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Properties of Constitutive Equations for Undilute Linear Polymers Based on the Molecular Theory

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The theoretical ideas of the viscoelasticity mechanism and the ways of their mathematical interpretation being developed simultaneously with the experimental studies are based on the construction of constitutive equations capable of describing the observed features of the viscoelastic behavior of a polymer system. Notwithstanding the considerable achievements of the nonstructural-phenomenological theories, it is obvious that the constitutive equations must be formulated by proceeding from principles based on the dynamics of individual macromolecules. This would enable one to relate the phenomenological constants of the theory to the specific characteristics of a macromolecular chain. The theoretical concepts of the viscoelasticity mechanism of a system of weakly coupled macromolecules have been discussed. The basic conclusions of the theory and its experimental verification bring to light the main features of the behavior of a macromolecule in an undiluted system (among other like macromolecules), namely: "to a first approximation" when perturbed a macromolecule moves in an undiluted system as in an after effect medium; the mean displacement of its center of gravity is of a monotonic and nonlinear nature, viz. the macromolecule is localized near its initial position-a scale of localization or an internal length appears.

Keywords: Constitutive equations; polymers; flow molecular theory

CONTENTS

1. INTRODUCTION

There is a really long history of the molecular approaches to the dynamic properties of a polymer system.

As regards dilute polymer solutions, the situation was cleared by 1960 owing to works by Kirkwood and Riseman (1948), Rouse (1953), Bueche (1954), Cerf (1958) and others. One of the main models known as the Rouse model of a macromolecule can be conceived as a set of Brownian particles in a viscous liquid linearly connected to one an other by elastic forces due mainly to entropy forces. It is well known that the Rouse model with properly defined hydrodynamic interaction, excluded volume effects, and internal viscosity is well consistent with experimental data.

The theory of dilute polymer solutions is the starting point of the theory of dynamical properties of non-dilute solutions and polymer melts that can be considered as a system of weakly-coupled macromolecules.

The viscoelastic behavior of such a system was the object of investigation of many groups in recent decades.

The strong elasticity of polymer solutions and melts was attributed initially to the network formed owing to temporary knots and/or entanglements. The network theory for the system was elaborated by Green and Tobolsky (1947), Lodge (1956), and Yamamoto (1956–1958).

Later the network concept was found to be wrong, nevertheless the concept of the intermediate length as the length between adjacent entanglements was retained in the reptation/tube theory advanced by de Gennes (1971) and Doi and Edwards (1978, 1979). The reptation concept was developed further in detail by many authors, but it appears to be inadequate to explain all the phenomena in polymer dynamics. A comprehensive discussion of the problem was given by Lodge *et al.* (1990). Despite the popularity of the theory of Doi and Edwards among rheologists, its predictions concerning several phenomena of pivotal significance such as the viscoelasticity of blends and the optical anisotrophy of slowly changing motions of macromolecules differ drastically from available data.

Below we discuss the theoretical concepts of the viscoelasticity mechanism of a system of weakly coupled macromolecules developed by Russian scientists beginning from the 1970s. The description of the dynamics of a macromolecule in the system is the corner stone of our theory. We do not assume that a macromolecule moves in a tube as it was done by de Gennes (1971) and Doi and Edwards (1986), nevertheless a scale of localization or an internal length appears in our theory. This localization scale can be interpreted as the radius of a "tube" containing a wriggling macromolecule. But calculations show that its possible reptations to approximations above the first order do not contribute substantially to relaxation processes underlying the main features of the viscoelastic behavior of a polymer liquid; the reptations must be considered when dealing with effects of "higher orders". Our theory is indeed a first approximation.

Below we shall consider the initial tenets and prerequisites of the molecular theory of the viscoelastic behavior of concentrated polymer solutions and melts, the basic nonlinear constitutive equations of the theory, and its corollaries for various cases of flow.

2. MACROMOLECULAR FOUNDATION OF CONSTITUTIVE EQUATION

2.1. Dynamics of a Macromolecule in a Concentrated System

To understand the mechanical behavior of an individual macromolecule in its motion among its kindred, it is sufficient to limit oneself to large-scale or slowly changing motions thereof. This makes it possible to model a macromolecule as a system of subchains. Such an approach was employed widely by many investigators when modeling the viscoelasticity and flow of polymers (Ferry, 1980 and Graessley, 1974). Each macromolecule is represented in the form of a chain of linearly bonded Brownian particles numbered from 0 to N and with the coordinates $r^0, r^1, \ldots, r^N$. The ν-th particle experiences the elastic force.

$$K_i^\nu = -2\mu T A_{\nu\gamma} r_i^\gamma, \tag{2.1}$$

where $\mu = 3N/2\langle R^2\rangle_0$, $\langle R\rangle_0$ is the mean-square end-to-end distance, T is the temperature in energy units, while matrix $A_{\nu\gamma}$ is a Rouse matrix and determines the bond of $N+1$ particles into a linear chain.

In the flow of a system, every Brownian particle moves in the flow with the velocity gradient

$$\nu_{ij} = \partial v_i / \partial x_j.$$

Using the symbols for a symmetrized and antisymmetrized tensor of the velocity gradients, we can write

$$\gamma_{ij} = \frac{1}{2}(\nu_{ij} + \nu_{ji}); \quad \omega_{ij} = \frac{1}{2}(\nu_{ij} - \nu_{ji}).$$

We can thus say that every Brownian particle experiences the effect of the additional forces of hydrodynamic drag F_i^α and internal friction G_i^α. The equation of motion of each of the particles can be written in the form of the Langevin equation:

$$m(d^2 r_i^\alpha / dt^2) = -\zeta r_i^\alpha + F_i^\alpha + G_i^\alpha + K_i^\alpha + \Phi_i^\alpha, \tag{2.2}$$

where $\Phi_i^\alpha(t)$ is a random process whose characteristics are defined from a fluctuating-dissipative expression (Pokrovskii and Pyshnograi, 1990).

Such an expression holds both for the motion of a macromolecule in a viscous liquid (in a very simple case $F = G = 0$) and for its motion among its kindred. In the latter case, the aftereffect must be considered in the expressions for the forces of external F_i^α and internal friction G_i^α respectively:

$$F_i^\alpha = -\int_0^\infty \beta(s)(r_i^\alpha - v_{ij} r_j^\alpha)_{t-s}\, ds,$$

$$G_i^\alpha = -\int_0^\infty \varphi(s)(r_i^\alpha - \omega_{kj} r_j^\alpha)_{t-s}\, ds, \tag{2.3}$$

the expressions in parentheses in the integrand were calculated for the $(t - s)$ moment of time.

One can readily see that the equation of dynamics (2.2) with the expressions for the forces (2.1) and (2.3) is the general form of the equation of the dynamics of a macromolecule in a flow to a linear approximation with respect to the coordinates and velocities of the particles. However, if the general form of the equation of dynamics (2.2) and (2.3) is written unambiguously in this case (a linear approximation), the memory functions in (2.3) cannot be established from general considerations. The involving of quite simple model considerations allowed Astarita and Marrucci (1974) to write the memory functions in the form

$$\beta(s) = (\zeta/\tau) B e^{-s/\tau}$$

$$\varphi(s) = (\zeta/\tau) E e^{-s/\tau} \tag{2.4}$$

As in Equation (2.2), in (2.4) ζ is the coefficient of friction of a Brownian particle in a "monomer" viscous liquid, and τ is a relaxation time of the surroundings that coincides with the calculated main time of mechanical relaxation (Pokrovskii and Volkov, 1978). In other words, the theory is self-consistent. The parameters B and E reflect the influence of the surroundings on the single molecule being considered. With a view to the nonlocal nature of the friction forces, one can estimate the change in these parameters depending on the length of the surrounding macromolecules M. For instance, Pokrovsky (1992) found that

$$B \approx M^{\delta}, \qquad \delta > 2. \tag{2.5}$$

Let us introduce the dimensionless parameters

$$\chi = \tau/2B\tau^* \quad \text{and} \quad \psi = E/B, \tag{2.6}$$

where $\tau^* = \zeta N^2/2T\mu\pi^2$ has the meaning of the characteristic time. From the physical viewpoint, τ^* is the maximum relaxation time of a macromolecule in a "monomeric" viscous liquid.

The theory being considered is featured by the absence of the usually postulated intermediate length that is like the chain length between entanglements of the macromolecules M_e, or tube diameter. It was understood lately that the localization of a macromolecule in "a tube" postulated by de Gennes follows from a formal approach based on Equations (2.2 – 2.4). An intermediate length appears that can be identified by the tube radius. Here

$$\chi = (2\zeta)^2/\langle R^2\rangle_0 \approx (M_e/M) \tag{2.7}$$

The last addend in the equation of dynamics (2.2) reflects the presence of a random heat force whose statistical properties, as usually (Chandrasekhar, 1943), are determined in such a way that in an equilibrium situation the quantities being calculated would coincide with known ones. With this definition of the random force, Equation (2.2) can be considered as a first approximation (linearity in coordinates, velocities, and velocity gradients) when describing nonequilibrium phenomena in undiluted polymers. With this approach, the effects associated with nonlinear addends, e.g. reptations (De Gennes, 1971) are eliminated. The latter appear with a different mobility of a particle along and across a chain and can be described by using addends higher than the first order.

2.2. Normal Modes and Morkov Form of Equation of Dynamics

For convenience of further calculations, we shall use transformed coordinates. They will be introduced with the aid of the orthogonal and normalized matrix Q

$$Q^T A Q = \lambda_\alpha E$$

$$\lambda_\alpha = (\pi\alpha/N^2); \ \alpha = 0, 1, 2, \ldots < N \tag{2.8}$$

By introducing the quantities transformed in this way and designated as

$$\rho_i^\alpha = Q^T r_i^\alpha; \ \psi_i^\alpha = Q^T \dot{r}_i^\alpha; \ \Gamma_i^\alpha = Q^T F_i^\alpha; \ T_i^\alpha = Q^T G_i^\alpha; \ f_i^\alpha = Q^T \Phi_i^\alpha \tag{2.9}$$

into the equation of dynamics (2.2), we obtain a system of differential equations (Pokrovskii and Pyshnograi, 1990).

$$d\rho_i^\alpha/dt = \psi_i^\alpha;$$

$$\mathrm{m}(d\psi_i^\alpha/dt) = -\zeta(\psi_i^\alpha - v_{ij}\rho_j^\alpha) + \Gamma_i^\alpha + T_i^\alpha - 2T\mu\lambda_\alpha\rho_i^\alpha + f_i^\alpha;$$

$$(d\Gamma_i^\alpha/dt) - v_{il}\Gamma_l^\alpha = (1/\tau)\Gamma_i^\alpha - (\zeta/\tau)B_{ij}(\psi_j^\alpha - v_{jl}\rho_l^\alpha);$$

$$(dT_i^\alpha/dt) - \omega_{il}T_l^\alpha = (1/\tau)T_i^\alpha - (\zeta/\tau)E_{ij}(\psi_j^\alpha - \omega_{jl}\rho_l^\alpha). \tag{2.10}$$

To achieve generality of the equation of dynamics of a macromolecule in both linear and nonlinear cases, in Equations (2.10) the scalars B_{ij} and E_{ij} were replaced by the tensor B and E, respectively. With a view to the monomolecular approximation, the medium in which a Brownian particle moves is assumed to be anisotropic (on an average), and the anisotropy is determined only by the extended macromolecular coils, i.e. by the tensor (Pyshnograi and Pokrovskii, 1988)

$$a_{ik} = \sum \langle \rho_i^\alpha \rho_k^\alpha \rangle / \langle \rho_j^\alpha \rho_j^\alpha \rangle_0 - \frac{1}{3}\delta_{ik},$$

where $\langle \rho_i^\alpha \rho_k^\alpha \rangle_0$ is the equilibrium value of the correlation moment $\langle \rho_i^\alpha \rho_k^\alpha \rangle$. The averaging is performed over the assembly of realizations of the random process f_i^α.

Hence, B_{ik} and E_{ik} are functions of the indicated tensor. In a linear approximation, the general form of the functions is as follows:

$$B_{ik} = B\left[\delta_{ik} - 3\beta\left(a_{ik} - \frac{1}{3}a_{ll}\delta_{ik}\right) - \kappa a_{ll}\delta_{ik}\right]$$

$$E_{ik} = E\left[\delta_{ik} - 3\varepsilon\left(a_{ik} - \frac{1}{3}a_{ll}\delta_{ik}\right) - \nu a_{ll}\delta_{ik}\right]. \tag{2.11}$$

The addends with constant β and ε determine the change in the coefficient of friction of a particle when the shape of the surrounding coils changes, and the addends with constant κ and ν when the volume of the coils changes (expansion).

Since at large velocity gradients the deformation of a coil cannot be considered small, linear approximation (2.11) is inadequate. For the more general case considered by Pokrovskii and Pyshnograi (1990), we can employ the convenient approximations

$$B_{ik} = B\left(\delta_{ik} + 3\beta\left(a_{ik} - \frac{1}{3}a_{ll}\delta_{ik}\right) + \kappa a_{ll}\delta_{ik}\right)^{-1}$$

$$E_{ik} = E\left(\delta_{ik} + 3\varepsilon\left(a_{ik} - \frac{1}{3}a_{ll}\delta_{ik}\right) + \nu a_{ll}\delta_{ik}\right)^{-1}. \tag{2.12}$$

At low changes of the size of a macromolecular coil, with an accuracy up to first-order terms with respect to the components of the anisotropy tensor, expressions (2.11) and (2.12) coincide.

2.3. Stresses in Deformation

A concentrated polymer solution or melt is a system of entangled chains. When modeling such a system in a monomolecular approximation, we consider that it can be represented in the form of a set of noninteracting macromolecules whose behavior is considered with a view to their neighbors. Each macromolecule is schematized by a chain with $N+1$ Brownian particles so that the system as a whole can be considered as a suspension of Brownian particles in a viscoelastic liquid. The set of Brownian particles can be characterized by the mean density.

$$\rho(x,t)=\sum_{\alpha}\mathrm{m}\langle\delta(x-r^{\alpha})\rangle=m(N+1)n(x,t) \qquad (2.13)$$

and the mean pulse density

$$\rho(x,t)v(x,t)=\sum_{\alpha}m\langle\dot{r}^{\alpha}\delta(x-r^{\alpha})\rangle \qquad (2.14)$$

The angular brackets signify averaging over the ensemble of realizations of the random forces in the equations of motion of the particles. Summation in (2.13) and (2.14) is performed over all the Brownian particles.

When formulating the equations of motion, which consists in deriving an expression for the stress tensor, one must consider the presence of two interacting continuums inserted into each other. They are formed by a carrying viscoelastic liquid and interacting Brownian particles which macromolecules are modeled by. However, the contribution of the carrying medium when dealing with a concentrated solution is insignificant and is no longer considered.

To find the stress tensor, we proceed from the determination of the pulse density (2.14) holding for an arbitrary set of Brownian particles.

By differentiating expression (14) with respect to time and employing quite simple transformations of Equation (2.2) (Pyshnograi and Pokrovskii, 1988), we obtain a standard form of the equation of motion of a continuum:

$$\rho(dv_i/dt)=(\partial\sigma_{ij}/\partial x_j)$$

where the stress tensor has the form

$$\sigma_{ij}=-nT\delta_{ij}+n\sum(2\mu\lambda_{\alpha}T\langle\rho_i^{\alpha}\rho_j^{\alpha}\rangle-m\langle\dot{\rho}_i^{\alpha}\dot{\rho}_j^{\alpha}\rangle-\langle\rho_j^{\alpha}T_i^{\alpha}\rangle) \qquad (2.15)$$

T^α_i is the transformed force of "internal" friction of a macromolecule determined according to (2.9).

Assuming a locally equilibrium distribution by velocities, we can write the stress tensor in the form:

$$\sigma_{ij} = -p\delta_{ij} + 3nT\sum_{\alpha}(x^\alpha_{ij} - \frac{1}{3}\delta_{ij} - u^\alpha_{ij}) \qquad (2.16)$$

The pressure p includes both the partial pressure of the gas of Brownian particles and $n(N+1)T$, and the pressure of a "monomer" liquid whose viscosity in our opinion could be ignored.

By the monomolecular approach, the stress tensor of a system is determined by the sum of the contributions of all the macromolecules, i.e. by simple multiplication by the number of macromolecules n.

In Equation (2.16), the stresses are determined by macroscopic mean values

$$x^\alpha_{ij} = \frac{2}{3}\mu\lambda_\alpha\langle\rho^\alpha_i\rho^\alpha_j\rangle, u^\alpha_{ij} = \frac{1}{3T}\langle\rho^\alpha_j T^\alpha_j\rangle \qquad (2.17)$$

that must be calculated.

The first group of variables in Equation (2.17) characterizes the size and shape of a macromolecular coil and is determined so that in equilibrium $x^\alpha_{ij} = 1/3\,\delta^\alpha_{ij}$.

The second group of variables is associated with the "internal" stresses appearing because each macromolecule is intertwined with its neighbors.

2.4. Relaxation Equations

To obtain determining equations, we must establish relaxation equations for the internal macroscopic parameters (2.17). To do this, we shall revert to the equation of the dynamics of a macromolecule in the form (2.10) with account taken of approximation (2.12). After transformations, we obtain a system of relaxation equations for the internal moments (Pokrovskii and Pyshnograi, 1991)

$$(D/Dt)\,x^{\alpha}_{ik}-(B\tau^{R}_{\alpha}/\tau_{\alpha})(x^{\alpha}_{ij}\gamma_{jl}c^{\alpha}_{lk}+x^{\alpha}_{kj}\gamma_{jl}c^{\alpha}_{lk})$$

$$=\frac{1}{2}\tau_{\alpha}\left(\left(x^{\alpha}_{ij}-\frac{1}{3}\delta_{ij}\right)b^{\alpha}_{jk}+\left(x^{\alpha}_{kj}-\frac{1}{3}\delta_{kj}\right)b^{\alpha}_{ji}\right);$$

$$(D/Dt)\,u^{\alpha}_{ik}-(B\tau^{R}_{\alpha}/\tau_{\alpha})\,e^{\alpha}_{ij}\gamma_{jl}u^{\alpha}_{lk}=-\left(\frac{1}{\tau}\delta_{ij}+\frac{1}{2}\tau_{\alpha}b^{\alpha}_{ij}\right)u^{\alpha}_{jk}$$

$$+\psi(B\tau^{R}_{\alpha}/\tau\tau_{\alpha})\left(\left(x^{\alpha}_{ij}-\frac{1}{3}\delta_{ij}\right)d^{\alpha}_{jk}-2B\tau^{R}_{\alpha}x^{\alpha}_{il}\gamma_{lj}f^{\alpha}_{jk}\right). \qquad (2.18)$$

The auxiliary quantities b^{α}_{ik}, c^{α}_{ik}, d^{α}_{ik}, e^{α}_{ik} and f^{α}_{ik} are determined in terms of the previously introduced parameters characterizing the dynamics of an individual macromolecule in a system

$$b^{\alpha}_{ik}=(\delta_{ik}-(B\tau^{R}_{\alpha}/\tau_{\alpha})(\beta_{ik}+\psi\varepsilon_{ik}))^{-1};$$

$$c^{\alpha}_{ik}=(\delta_{ij}-\beta_{ij})\,b^{\alpha}_{jk};\;\; e^{\alpha}_{ik}=b^{\alpha}_{ij}(\delta_{ji}-\beta_{jk});$$

$$d^{\alpha}_{ik}=b^{\alpha}_{ij}(\delta_{kj}-\varepsilon_{kj});\; f^{\alpha}_{ik}=c^{\alpha}_{ij}(\delta_{kj}-\varepsilon_{kj});$$

$$\beta_{ik}=3\left(\frac{1}{3}\kappa a_{ll}\delta_{ij}+\beta\left(a_{ij}-\frac{1}{3}a_{ll}\delta_{ij}\right)\right)\left(\delta_{jk}+\left(\kappa a_{ll}\delta_{jk}+3\beta\left(a_{jk}-\frac{1}{3}a_{ll}\delta_{jk}\right)\right)\right)^{-1};$$

$$\varepsilon_{ik}=3\left(\frac{1}{3}\nu a_{ll}\delta_{ij}+\varepsilon\left(a_{ij}-\frac{1}{3}a_{ll}\delta_{ij}\right)\right)\left(\delta_{jk}+\left(\nu a_{ll}\delta_{jk}+3\varepsilon(a_{jk}-\frac{1}{3}a_{ll}\delta_{jk}\right)\right)^{-1}.$$

The system of relaxation equations includes the relaxation times

$$\tau;\tau_{\alpha}=\tau/2+B\tau^{R}_{\alpha}(1+\psi),\tau^{R}_{\alpha}=\tau^{*}/\alpha^{2} \qquad (2.19)$$

The relaxation processes by (2.18) are featured, particular, by anisotropy of relaxation, viz. in a deformed system different components of the tensors x^{α}_{ik} and u^{α}_{ik} relax at a different rate.

We shall consider below the conclusions of the theory and its applications for various cases of deformation.

2.5. Discussion of the Approach

Initially our concept was based on some rather formal approaches of macromolecule dynamics and some suggestions of a general kind (Pokrovskii and Volkov, 1978). Later the picture of thermal motion of macromolecules in non-dilute system was clarified step by step (Pokrovskii and Kokorin, 1985, 1987). The thermal motion is featured by localization of a macromolecule near its initial position. Figure 1. shows the displacement of a macromolecule and the intermediate length ξ that is similar to the length ξ between adjacent entanglements. The motion of macromolecule is so constrained by the surrounding chains that its motion is essentially equivalent to the motion of the macromolecule in an effective tube. But this does not mean that there is reptation inside the tube.

We can discuss this in more detail as answers to the questions posed by Lodge *et al.* (1990, p. 16–17).

1. Do linear polymer chains execute primarily reptation over a non-vanishing region of parameter space?

No. Reptation is a very weak effect that can be manifest in special cases noted by Lodge *et al.* (1990, p. 117) as strict reptation: "sufficiently long tracer chains surrounded by a matrix of much longer

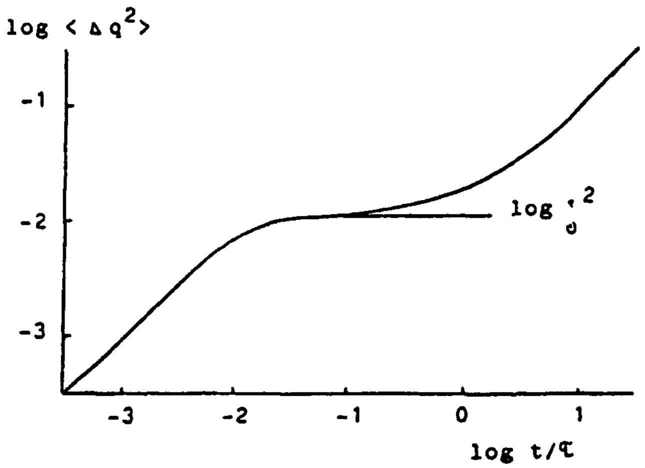

FIGURE 1 The displacement of the center of mass of a macromolecule depends on the intermediate length ξ-scale. The displacement is measured in units of $(\tau\langle R^2\rangle/\pi^2\tau^*)^{1/2}$.

chains, and unattached chains in a regular network". It is incorrect to consider reptation as a first approximation of the theory of relaxation of macromolecules.

*What is fundamentally incorrect in the reptation model?

The postulation of reptation as the main form of thermal motion of macromolecules is incorrect.

*What is the strongest evidence against reptation?

The strongest evidence against reptation is the discrepancies of the results for the viscoelasticity of a dilute blend of a linear polymer (Yanovsky *et al.* 1980, Vinogradov *et al.* 1982, Pokrovskii and Kokorin 1985, Yonovsky 1993).

*What is the most promising alternative approach?

We most likely set out the best monomacromolecular approach that includes all the features of behavior of linear polymers.

The Schweizer's (1989a, 1989b, 1991) monomacromolecular approach is naturally better, but it is not completed yet.

*Why does the reptation picture seem to agree with so many observations?

Some effects are consequences not of reptation, but of constraints of motion with on internal length postulated in the reptation, theory that appears in our theory as a localization effect. Besides, the reptation theory has its region of validity pointed out by Lodge *et al.* (1990, p. 117).

2. What further experiments, if any, are required to answer question 1 without any reasonable doubt?

A comparison of dynamic birefringence and the dynamic modulus. Investigation of birefringence and viscoelasticity of a dilute blend of polymers. The predictions of the reptation theory and our theory are quite different (Pokrovskii and Kokorin, 1985, 1987).

3. In what direction should future theoretical efforts be aimed?

The main direction of future theoretical efforts should be investigation of multimacromolecular approaches.

These are replies to the questions of Lodge *et al.* (1990, p. 16–17).

Despite the continuing research into the problem there is no evidence of any conflict between the large volume of experimental data that has now accumulated and the discussed theory.

3. UNIFORM MOTION WITH LOW VELOCITY GRADIENTS

System of Equations (2.16) and (2.18) determines the stresses in a polymer liquid as functions of velocity gradients, in other words system of Equations (2.16) and (2.18) is a constitutive equation of a polymer liquid that was formulated by proceeding from principles based on the dynamics of individual macromolecules. To compare the theoretical predictions with experimental results, let us first consider low velocity gradients.

3.1. Dynamic Modulus

The viscoelastic behavior of a polymer system is manifest in the most typical way in uniform oscillating motion

$$v_{12} \sim e^{-i\omega t}$$

The expressions for the stresses and moments in a linear case also determine the expression for the dynamic modulus, which in the general case has the form (Yanovsky *et al.* 1988, Pokrovskii 1992, Yanovsky 1993)

$$G^*(\omega) = nTf(\tau^*\omega, B, \chi, \psi). \tag{3.1}$$

The frequency dependence of the dynamic modulus is shown in Figure 2 and in the approximation considered here (at low frequencies) is determined by relaxation processes with two sets of relaxation times whose values are determined by Equations (2.18)

$$\tau_\alpha = B\tau^*[\chi + \alpha^{-2}(1+\psi)], \quad \tau_\alpha^0 = 2\tau\tau_\alpha/(\tau + 2\tau_\alpha). \tag{3.2}$$

It should be noted that the indicated curve has two relaxation branches. The one with slower relaxation processes due to the change in the average size of a macromolecule is hardly manifest on the frequency dependence of the dynamic modulus, though the reptation relaxation processes ought to be identified exactly with this branch.

The intermediate plateau in the modulus is associated with the intermediate length

$$G_e = \frac{\pi^2}{12} nT\chi^{-1}. \tag{3.3}$$

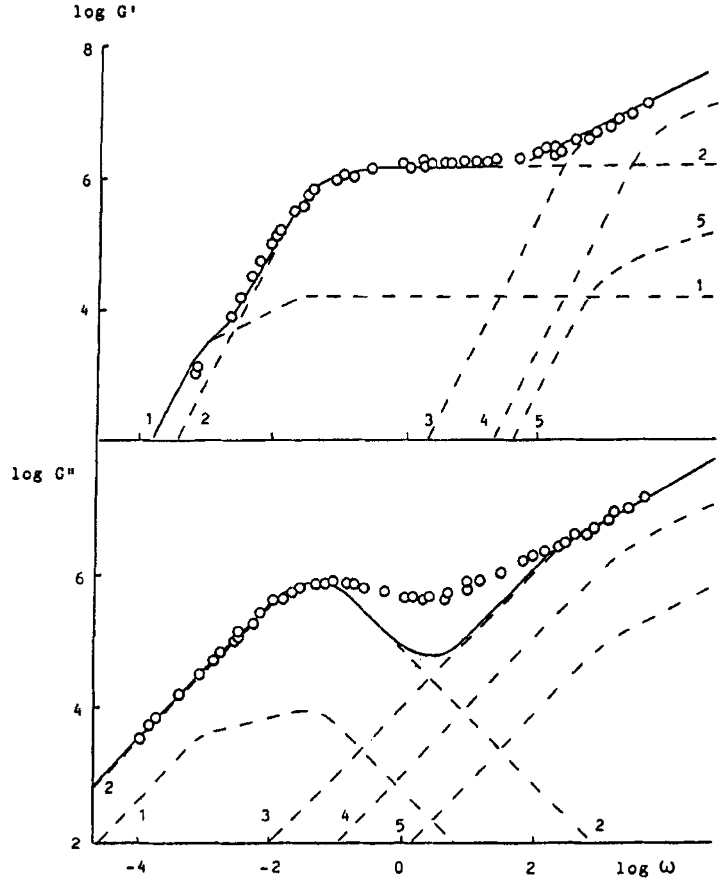

FIGURE 2 Experimental and theoretical frequency dependences of the real G' and imaginary G'' components of the dynamic shear modulus. The points were reproduced from Onogi, S. *et al.* (1970) for polystyrene with a molecular weight of 215000 at 160°C. The theoretical values indicated by the dashed lines were calculated for values of $B = 3 \times 10^6$; $E = 2 \times 10^4$; $\chi = 0.08$; $\tau^* = 5 \times 10^{-5}$s and $nT = 1.7 \times 10^5$ dyn. cm^{-2}.

It is clear from the picture that the main relaxation branch is the one numbered 2. Its set of relaxation times (3.2) is not wide and can be approximated with a single relaxation time τ that coincides with the introduced relaxation time τ. Hence at $\psi \to \infty$ we have self-consistency without any extra requirement. The requirement of the equality of relaxation times of macro- and microviscoelasticity gives a first order a relation with respect to ψ^{-1}

$$\psi = \frac{4}{\pi^2}\chi^{-1} \tag{3.4}$$

Recently Leonov (1994) attempted to improve the theory by focusing on the formulation of the true self-consistency condition for the model, that is the requirement of equality of the micro- and macroviscoelasticities.

However, simple reasoning shows that "the true self-consistency condition" cannot be reached. Indeed, a macromolecule in a viscous fluid gives one set of relaxation times, in a fluid with one relaxation time gives a several sets of relaxation times, and so on. That is why in our papers we stopped using the "true self-consistency condition" and discussed the correlation between the relaxation times of micro and macroviscoelasticity. A self-consistency condition of this kind was discussed by Pokrovskii (1992).

3.2. Steady Simple Shear

In steady shear, to a first approximation according to the velocity gradient, only the shear differs from zero:

$$\sigma^0_{12} = \eta_0 \nu_{12}; \ \eta_0 = \frac{\pi}{6} n T B \tau^*. \tag{3.5}$$

Approximations of a higher order reveal that normal stresses are also needed to realize shear strain. For low values of the parameters χ, ψ and β (here $\beta = \kappa, \varepsilon = \nu$), it was found that (Pokrovskii and Kokorin, 1985)

$$\begin{gathered}
\sigma_{12} = \eta \nu_{12} \\
\eta = \eta_0 \left[1 - \left(\frac{\sigma^0_{12}}{nT} \right)^2 \left(\frac{72}{315}\psi + \frac{72}{15}\pi^2 \chi \right) \right] \\
\sigma_{11} + p = nT\left(\frac{\pi^4}{45} + \frac{\pi^2}{6}\chi - \frac{\pi^4}{90}\beta \right)(B\tau^* \nu_{12})^2 \\
\sigma_{22} + p = nT\left(\frac{\pi^2}{6}\chi + \frac{\pi^4}{90}\beta \right)(B\tau^* \nu_{12})^2 \\
\sigma_{33} + p = 0
\end{gathered} \tag{3.6}$$

In summarizing the results obtained in (3.4), we must note three factors causing the appearance of nonlinear effects in shear, namely, (i) the effective nonlinear rigidity of a macromolecule (ψ), (ii) the after-effect of the surroundings (χ), and (iii) the effects connected with a change in the size and shape of the macromolecular coils (β).

We can obtain relations for shear strain from expressions (3.4):

$$\sigma_{11}-\sigma_{33}=\frac{1}{nT}\left(\frac{4}{5}+\frac{6}{\pi^2}\chi-\frac{4}{10}\beta\right)\sigma_{12}^2$$

$$\frac{\sigma_{22}-\sigma_{33}}{\sigma_{11}-\sigma_{33}}=-\frac{15}{2\pi^2}-\frac{1}{2}\beta \tag{3.7}$$

They can be verified experimentally. By data typical for concentrated polymer systems (Graessley, 1974), the first difference of the normal stresses $\sigma_{11}-\sigma_{33}$ is proportional to the square of the shear stresses in the region of low velocity gradients. The second difference of the normal stresses $\sigma_{22}-\sigma_{33}$ is low in comparison with the first one, which conforms with the previous statement on the smallness of the parameters β and χ.

3.3. Extentional Flow

Steady uniaxial extentional flow is studied on the basis of Equations (2.16) and (2.18).

Stickfort (1986) showed that the steady extentional viscosity could be represented vs. the shear stress σ as follows:

$$\lambda(\sigma)=\frac{3}{2\gamma(\sigma)}\cdot\frac{1}{1-\frac{1}{3}\alpha(\sigma)\sigma}$$

where $\gamma(\sigma)$ and $\alpha(\sigma)$ are phenomenological functions, the slip and anisotropy of the flow coefficients, respectively. On the basis of the constitutive Equations (2.16) and (2.18), Pyshnograi (1994) calculated the first terms in the series of $\gamma(\sigma)$ and $\alpha(\sigma)$ by degrees of tensile stresses. With precision of the second order with respect to σ, we have

$$\gamma(\bar{\sigma}) = \gamma_0\left(1 - \frac{16}{525}\left(\frac{4}{3} - 11\beta\right)\bar{\sigma}^2\right)$$

$$\alpha(\bar{\sigma}) = \frac{2\pi^2}{15}\cdot\frac{\gamma_0^2}{\gamma(\bar{\sigma})}\left(1 - 3\beta - \frac{4}{3}\left(\frac{8}{105} + 7\beta\right)\bar{\sigma}^2\right) \tag{3.8}$$

where $\gamma_0 = 3/\pi^2 nTB\tau^*$ and $\bar{\sigma} = \sigma/nT$.

This relations correspond to the information given by Stickforth (1986) on the functions $\gamma(\sigma)$ and $\alpha(\sigma)$, which was obtained from experimental data. The last relation in (3.8) determines the relation between the phenomenological (macro) anisotropy and microanisotropy coefficient β.

4. CONSTITUTIVE EQUATION FOR FLOWABLE SYSTEM

It can be seen from the preceding section that the system of constitutive Equations (2.16) and (2.18), notwithstanding the simplifying assumptions, is quite cumbersome. To facilitate further calculations, it is expedient to employ additional assumptions, in particular, low values of some parameters of theory. (It must be stressed, however, that in principle the investigation of a quite general case is also possible.)

4.1. Condition of Flowability

The irreversible flow of a system becomes appreciable for observation times longer than the relaxation times of a macromolecule, the longest of which is, according to (3.2)

$$\tau_1 = \tau(1 + \chi + \psi)/2\chi \tag{4.1}$$

In analyzing the system of equations, we can note that the parameter χ by the meaning of the problem posed [see expression (2.7)] changes within the range of values from 0.01 to 0.1 We can consider it to be small with adequate grounds. At the same time, the parameter ψ may have either large or small values, which corresponds to two different cases of behavior of the system. At large values of ψ and low velocity gradients, the relaxation times [see Equation (3.2)] of the first set of variables considerably exceed the relaxation times of the second set, for which $\tau_\alpha^0 = \tau$ holds in this case. Actually, these relaxation times are manifest as a single main one-the most noticeable relaxation time determining the viscoelastic behaviour of a system as a whole. Since the relaxation processes with the first set of relaxation times contribute only slightly to the stresses, i.e. are actually not noticeable, the durations of flow are compared with the relaxation time τ and the system is perceived as a nonflowing one.

In the other limit case when $\psi \ll 1$, the systems are perceived as flowing ones. This case is the most interesting for applications connected, in particular, with the theory of polymer article molding.

Since for cases of flow, the system of Equations (2.16) and (2.18) can be simplified because of the low values of the parameters χ and ψ, we shall discuss below the results obtained exactly in the approximation to first-order terms with respect to χ and ψ.

4.2. Zero-Order Approximation

We shall now discuss the possible simplification of the indicated expressions with respect to χ and ψ holding for any arbitrary velocity gradients. In this case from Equations (2.16) and (2.18) in the zero approximation in parameters χ and ψ we obtain a system of constitutive relations.

Then we retain the only internal variable characterizing the highest relaxation times and obtain relations for the stress tensor and an equation for the internal variable.

$$\sigma_{ij} = -p\delta_{ij} + 3\frac{h_0}{\tau_0}\left(\xi_{ij} - \frac{1}{3}\delta_{ij}\right)$$

$$\frac{d\xi}{dt} - v_{il}\xi_{ij} - v_{ji}\xi_{li} = -\frac{1}{\tau_0}(1 + (\kappa - \beta)\xi_{ss})\left(\xi_{ij} - \frac{1}{3}\delta_{ij}\right)$$

$$- 3\frac{\beta}{\tau_0}\left(\xi_{il} - \frac{1}{3}\delta_{il}\right)\left(\xi_{lj} - \frac{1}{3}\delta_{lj}\right) \tag{4.2}$$

The system includes the characteristics of the material: η_0 is the initial shear viscosity, τ_0 is the initial relaxation time, κ and β determine the effect of changing of the volume (κ) and form (β) of a molecular coil on the macromolecule dynamics.

One of the properties of constitutive Equations (4.2) is the anisotropy of relaxation: different components of the tensor ξ_{il} approach equilibrium at a different rate. When anisotropy is disregarded ($\beta = 0$), system of Equations (4.2) takes on a simpler form

$$\sigma_{ij} = -p\delta_{ij} + 3\frac{\eta}{\tau}\left(\xi_{ij} - \frac{1}{3}\delta_{ij}\right)$$

$$\frac{D\xi_{ij}}{Dt} - \gamma_{il}\xi_{lj} - \gamma_{jl}\xi_{li} = -\frac{1}{\tau D}\left(\xi_{ij} - \frac{1}{3}\delta_{ij}\right) \tag{4.3}$$

$$\tau D = \frac{\tau_0}{1 + \kappa D/3}; \quad a_{ss} = \xi_{ss} - 1.$$

The quantity η in system (4.3) has the meaning of the shear viscosity coefficient and depends on the invariance of the tensor a_{ij} in the same way as the relaxation time

$$\frac{\eta}{\eta_0} = \frac{\tau}{\tau_0} = \left(1 + \frac{1}{3}\kappa D\right)^{-1} = \varphi(D) \tag{4.4}$$

The subscript "0" signifies the initial (independent of the argument) values of the relevant quantities.

The argument of the shear viscosity coefficient and relaxation time in the approximation being considered has the meaning of the first invariant of the tensor of additional stresses

$$D = 3a_{ss} = 3(\xi_{ss} - 1) = \frac{\tau_0}{\eta_0}(\sigma_{ss} + 3p) \tag{4.5}$$

Consequently, in a very simple variant, the system of determining Equations (4.3)–(4.5) contains two rheological parameters: the initial shear viscosity η_0 and the initial relaxation time τ_0, as well as the dimensionless function $\varphi(D)$.

4.3. Steady Simple Shear

In practice, the properties of a polymer liquid were mainly studied by uniform shear, that is, only one component of the gradient rate tensor differs from 0, namely, $v_{12} \neq 0$. However in analyzing the shear deformation of viscoelastic media, we have to take into account not only the tangential stresses σ_{12}, as for linear viscoelastic liquids, but also the normal stresses. The latter can be set as the difference of the normal stresses $\sigma_{11} - \sigma_{22}$ and $\sigma_{22} - \sigma_{33}$. The stresses under consideration are defined as

$$\sigma_{12} = \eta v_{12}; \quad \sigma_{11} - \sigma_{22} = \Psi_1 v_{12}^2; \quad \sigma_{22} - \sigma_{33} = \Psi_2 v_{12}^2 \tag{4.6}$$

In a theoretical interpretation of the coefficients of shear viscosity η and normal stresses Ψ_1 and Ψ_2, in general, one can assume $\beta \neq 0$. In this case the system of Equations (2.2) defines the above coefficients as functions of the gradient rates.

Figures 3, 4 shows the steady shear viscosity η versus the dimensionless shear rate $\tau_0 v_{12}$ for various values of the parameters κ and β. The curves in Figure 3 show that as β increases, the deviation of η from η_0 also increases. It should be noted that variation of the parameter κ has

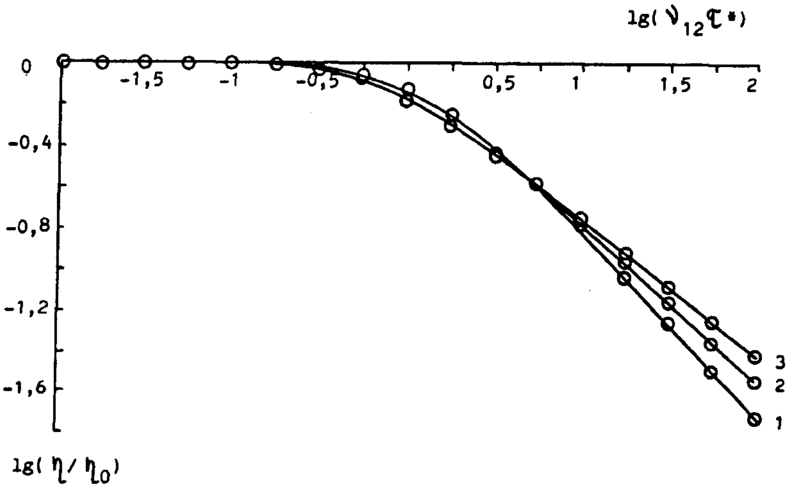

FIGURE 3 Viscosity vs. shear rate for different values of the parameter κ:1 — 0.2; 2 — 0.3; 3 — 1.0. $\beta = 0.2$.

a small affect on the values of the viscosimetric functions. Figure 5 shows the shear stress versus the dimensionless shear rate for various values of the parameters β. If $\beta < \kappa$, the value of the shear stress is an

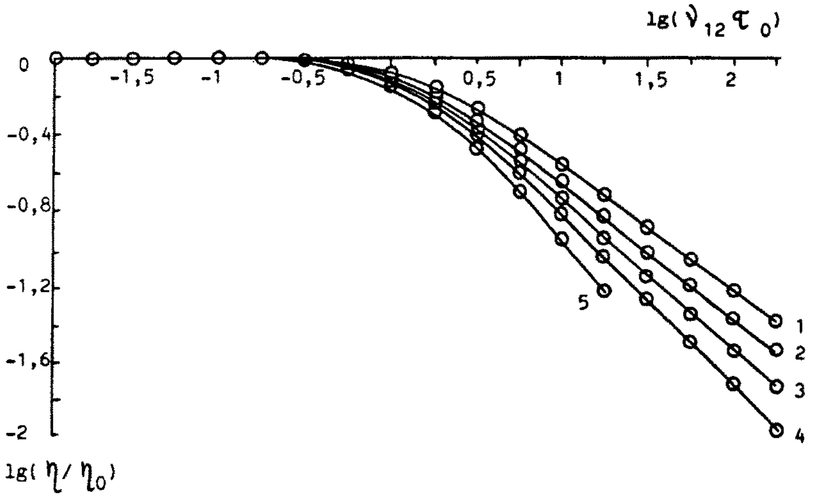

FIGURE 4 Viscosity vs. shear rate for different values of the parameter β:1 – 0.05; 2 – 0.1; 3 – 0.15; 4 – 0.2; 5 – 0.3. $\kappa = 0.2$.

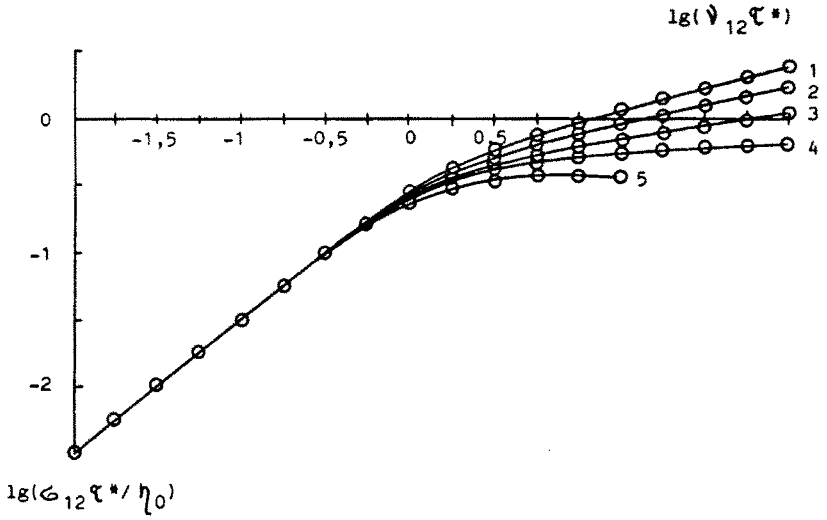

FIGURE 5 Shear stress vs. shear rate for different values of the parameter β (see Fig. 4 for the curves). $\kappa = 0.2$.

increasing function of the shear rate that is consistent with experimental data.

In Figure 6, the first normal stress coefficient Ψ_1 is plotted versus the shear rate and diminishes when the latter grows.

The dependence of the ratio of the second normal stress difference to the first one Ψ_2/Ψ_1 is given in Figure 7. This ratio is negative and decreases depending on the magnitude of a function of the dimensionless shear rate. This also agrees with experimental data.

If the gradient rates are small, the parameters η, Ψ_1 and Ψ_2 with a second order approximation can be written as follows:

$$\eta = \eta_0\left[1 - \frac{1}{3}(2\kappa + 7\beta)\right]; \quad \Psi_1 = 2\eta_0\tau_0; \quad \Psi_2 = -\beta\eta_0\tau_0 \qquad (4.7)$$

Comparison of the theoretical calculated data (Figs. 3–7) and the experimental results shows that the above theory gives sufficiently reliable relations, observed experimentally. Particularly, the second difference of normal stresses is negative and small in comparison with

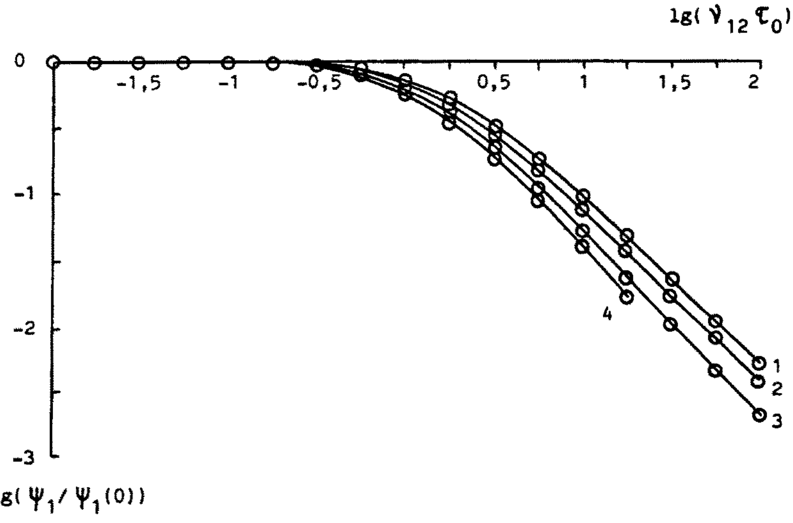

FIGURE 6 First normal stress coefficient vs. the shear rate for different values of the parameter β:1 – 0.05; 2 – 0.1; 3 – 0.2; 4 – 0.3. $\kappa = 0.2$ β:1 – 0.05; 2 – 0.1; 3 – 0.2; 4 – 0.3. $\kappa = 0.2$.

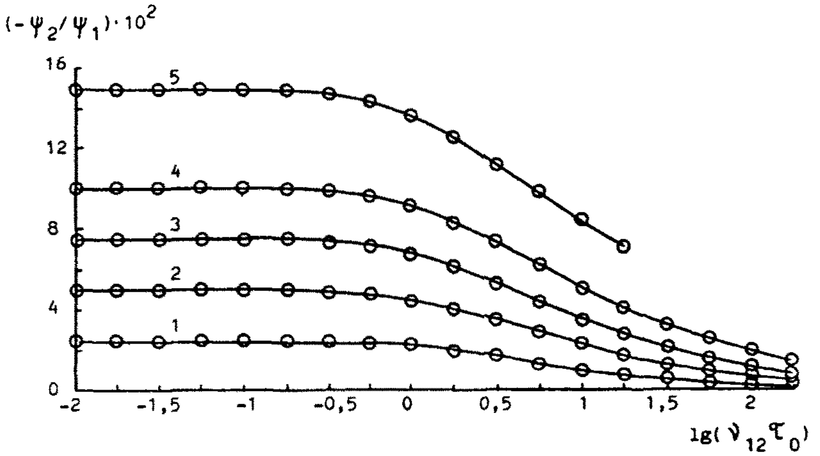

FIGURE 7 Ratio of the second normal stress difference to the first one vs. the shear rate for different values of the parameter β (see Fig. 4 for the curves). $\kappa = 0.2$.

the first one (Graessley, 1974). It shows the anisotropy coefficient to be a small quantity.

At small magnitudes of the gradient rates, the ratio of the normal stress difference depends only on the coefficient anisotropy:

$$\frac{\sigma_{22}-\sigma_{33}}{\sigma_{11}-\sigma_{33}} = -\frac{1}{2}\beta \tag{4.8}$$

Figure 7 shows such a ratio for an arbitrary value of the gradient rate.

In the zero approximation of a viscoelastic flow, the ratio of the normal stress difference should not depend on the macromolecule length.

For experimental verification of the above inference, one must obtain the value of this ratio for samples characterized well by the molecular parameters. Unfortunately, in vien of the problems connected with difficulties of measuring the second normal stress difference investigations of this kind still remain incomplete.

One can notice that when $\beta = 0$ of simple shear, the following expressions can be obtained from systems (4.3)

$$\eta = \eta_0 \bigg/ \left(1 + \frac{1}{3}\kappa D\right); \quad \tau = \tau_0 \bigg/ \left(1 + \frac{1}{3}\kappa D\right); \quad \Psi_1 = 2\eta\tau; \quad \Psi_2 = 0; \tag{4.9}$$

where $D = \tau_0/\eta_0(\sigma_{ss} + 3p)$ is the first dimensionless invariant of the additional stress tensor.

Expressions (4.9) are more approximate in comparison with (4.6) and (4.7).

4.4. Relation Between Shear and Extentional Viscosity Coefficients

Consider the case of employing system (4.3) for describing the uniaxial tension of a polymer liquid with an extentional viscosity coefficient λ (λ is determined by the ratio of the tensile stress σ to the velocity gradient v_{11}). We shall calculate the ratio between the coefficients of extentional λ and shear viscosity η, namely, the quantity λ/η by using system of Equations (4.2). For uniform uniaxial tension of a polymer liquid along axis 1, the tensor of the velocity gradients (the values of v_{11} do not depend on the coordinates) with a view to the conditions of incompressibility can be written in the form

$$v_{ik} = \begin{Vmatrix} v_{11} & 0 & 0 \\ 0 & -\frac{1}{2}v_{11} & 0 \\ 0 & 0 & -\frac{1}{2}v_{11} \end{Vmatrix}$$

Excluding the pressure from the relations for the stresses [see system of Equations (4.3)] because we are considering uniaxial tension, we obtain an expression for the tensile stress

$$\sigma = 3\frac{\eta}{\tau}(\xi_{11} - \xi_{22}) = 3\eta(2\xi_{11} + \xi_{22})v_{11} \tag{4.10}$$

where

$$\xi_{ii} = \frac{1}{3} + \frac{2\tau v}{1 - 2v_{ii}\tau} \tag{4.11}$$

The tensile stress in the steady case characterizes the apparent extentional viscosity

$$\lambda \doteq 3\frac{\eta}{1 - \tau v_{11} - 2(\tau v_{11})^2} \tag{4.12}$$

Figure 8 shows the steady extentional viscosity λ versus the dimensionless elongational rate $v_{11}\tau_0$ for different values of the parameters $\kappa = \beta$. Here the extentional viscosity increases with the extentional rate.

The viscosity coefficients η and λ are functions of the first invariant of the tensor of stresses

$$D = \frac{\tau_0}{\eta_0}(\sigma_{ii} + 3p)$$

which with the aid of expressions (4.7) and (4.8) is written in terms of the velocity gradient

$$D = \frac{\lambda}{\eta}2(\tau v_{11})^2 \tag{4.13}$$

Analysis of expressions (4.9) and (4.10) enables us to obtain an expression for the ratio of the coefficients of extentional and shear viscosity

$$\frac{\lambda}{\eta} = 3 + \frac{5}{4}D + \sqrt{\left(\frac{3}{2}D + \frac{9}{16}D^2\right)} \tag{4.14}$$

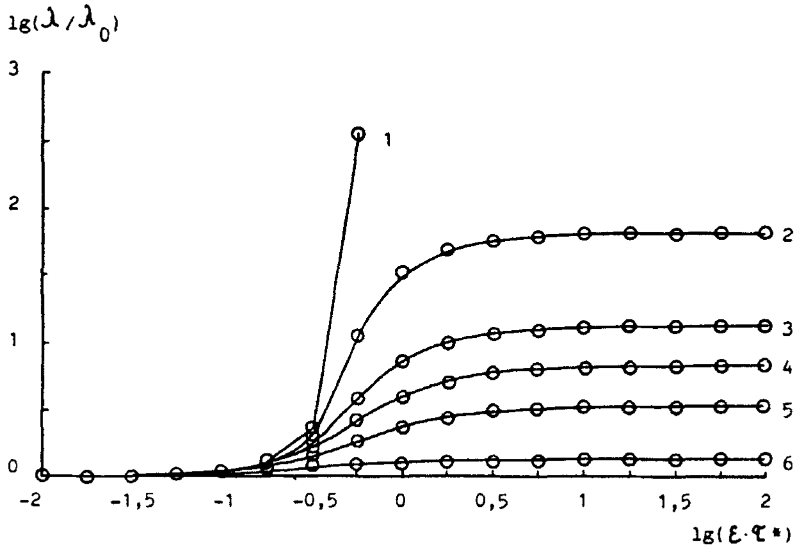

FIGURE 8 Elongational viscosity vs. elongational rate for different values of the parameter $\beta = \kappa$:1 – 0.0; 2 – 0.01; 3 – 0.05; 4 – 0.1; 5 – 0.2; 6 – 0.5.

For shear strain, the invariant D has the form:

$$D = 2\left(\frac{\tau_0}{\eta_0}\sigma_{12}\right)^2 \tag{4.15}$$

and for uniaxial tension

$$D = \frac{1}{2}\left[-3 - \frac{\tau_0}{\eta_0}\sigma + \left(9 + 6\frac{\tau_0}{\eta_0}\sigma + 9\left(\frac{\tau_0}{\eta_0}\sigma\right)^2\right)^{\frac{1}{2}}\right] \tag{4.16}$$

It should be noted that when deriving expression (4.14) we used the assumption that η and λ are functions of D, but we did not give the specific form of this function.

Expression (4.14) makes it possible to see whether the system of equations (2.3) discussed above can be employed to describe flows of polymer liquids differing in their nature.

Figure 9 presents experimental values of λ/η depending on D for numerous polymer system in comparison with theoretical calculations by formula (4.16). The experimental results can be seen to have a definite scatter relative to the theoretical curve, which can be ascribed to both natural experimental errors and the necessity of introducing theoretical corrections associated with the parameters χ and Ψ. However, the observed consistence of the experimental and theoretical appraisals can be considered satisfactory. This points to the possibility of employing the proposed theoretical relations for describing the properties of various types of polymer systems.

We draw attention to the fact the expression (4.12) equals infinity when $v_{11} = 1/2\tau$. This feature has no real physical meaning, but is connected with the fact that expression (4.12) holds for small tensions and, consequently, for low velocity gradients, when the following condition is observed for the velocity gradient:

$$2\tau v \ll 1$$

or an equivalent condition is observed for the applied stress

$$\frac{\tau_0}{\eta_0}\sigma \ll \frac{1}{2}\frac{\lambda}{\eta}$$

The values of λ/η calculated by formulas (4.14) for large stress values approach the boundary of the applicability region asymptotically.

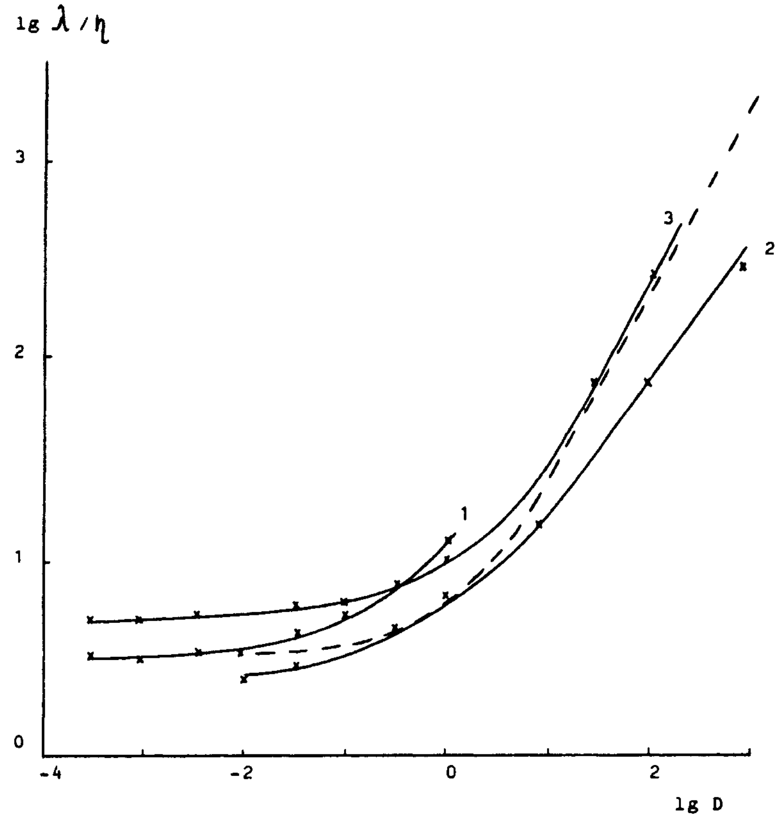

FIGURE 9 Theoretical (dashed line) and experimental (solid lines) dependences of the ratio of the longitudinal and shear viscosity coefficients on the invariant tensor of additional stresses for the systems listed in the table.

Hence, theory does not lead to infinite stresses that may exceed the actually observed ones. The use of Equation. (4. 14) with large stress values also has restrictions because of an initial prerequisite introduced into the theory, namely, on the unlimited stretching of a macromolecule. This condition is naturally not observed in a real situation because a macromolecule can stretch only to a certain limit.

4.5. Nonsteady Simple Shear

To consider the problem, let us compile constitutive equations for small velocity gradients. In this case, we consider a quite simple case when the nonlinear effects are associated only with a change in the volume of the macromolecular coils. In expressions (2.18), the values of $\beta = \varepsilon = 0$ correspond to this condition. We can see here that the effects connected with anisotropy of relaxation are eliminated, and the system of relaxation equations acquires the form:

$$\tau_\alpha(Dx^a_{ik}/Dt) - [B\tau^R_\alpha/(1+\kappa a_{ss})](\gamma_{il}x^\alpha_{ik} + \gamma_{kl}x^\alpha_{li}) = -(x^\alpha_{ik} - \frac{1}{3}\delta_{ik}) \quad (4.17)$$

$$\tau^0_\alpha(Du^a_{ik}/Dt) - [B\tau^R_\alpha/(1+\kappa a_{ss})](\tau^0_\alpha/\tau_\alpha)\gamma_{il}u^\alpha_{lk}$$

$$= u^\alpha_{ik} - (B\tau^R_\alpha/(1+\kappa a_{ss}))(E\tau^R_\alpha/(1+\nu a_{ss}))(2\tau^0_\alpha/\tau\tau_\alpha)\gamma_{il}x^\alpha_{lk}$$

$$+ (E\tau^R_\alpha/(1+\nu a_{ss}))(\tau^0_\alpha/\tau\tau_\alpha)(x^\alpha_{ik} - \frac{1}{3}\delta_{ik}) \quad (4.18)$$

where the following values are used for the relaxation times:

$$\tau_\alpha = \tau/2 + \tau^R_\alpha(B/(1+\kappa a_{ss}) + E/(1+\nu a_{ss})$$

$$\tau^0_\alpha = (2\tau\tau_\alpha)/(\tau + 2\tau_\alpha); \quad \tau^R_\alpha = \tau^*/\alpha^2;$$

Equations (2.16), (4.17) and (4.18) form a system of constitutive equations of a linear polymer with two sets of internal relaxation variables.

According to the structure of Equation (4.19), the quantities u^α_{ik} are proportional to E, hence in the indicated equation we can assume that

$$\tau_\alpha = (B\tau^R_\alpha)/(1+\kappa a_{ss}); \quad \tau^0_\alpha = \tau \quad (4.19)$$

This enables us to write the following expression instead of (4.18)

$$\tau(Du^\alpha_{ik}/Dt) - \tau\gamma_{il}u^\alpha_{lk} = -u^\alpha_{ik} + \psi[(1+\kappa a_{ss})/(1+\nu a_{ss})]\left(x^\alpha_{ik} - \frac{1}{3}\delta_{ik}\right)$$

$$-2\psi[(1+\kappa a_{ss})/(1+\nu a_{ss})](\tau_\alpha\gamma_{il}x^\alpha_{lk}); \quad (4.20)$$

and hence the system of equations (2.16), (4.17) and (4.20) with an accuracy within first-order terms with respect to χ and Ψ is exactly a system of constitutive equations for flowing polymer systems.

As an example confirming the possibilities of employing the above expressions for practical estimates, we shall compare the results of theoretical calculations with experimental ones. This is shown in Figure 10 in the form of a plot of the shear stresses vs. the shear strain. (It should be noted that the normal stresses evaluated for this case also vary nonmonotonically (Grebnev and Pokrovskii, 1987). The comparison of the experimental and theoretical relations (Fig. 10) can be considered as satisfactory only for comparatively low velocity gradients. This is not surprising, by the way, because considerable

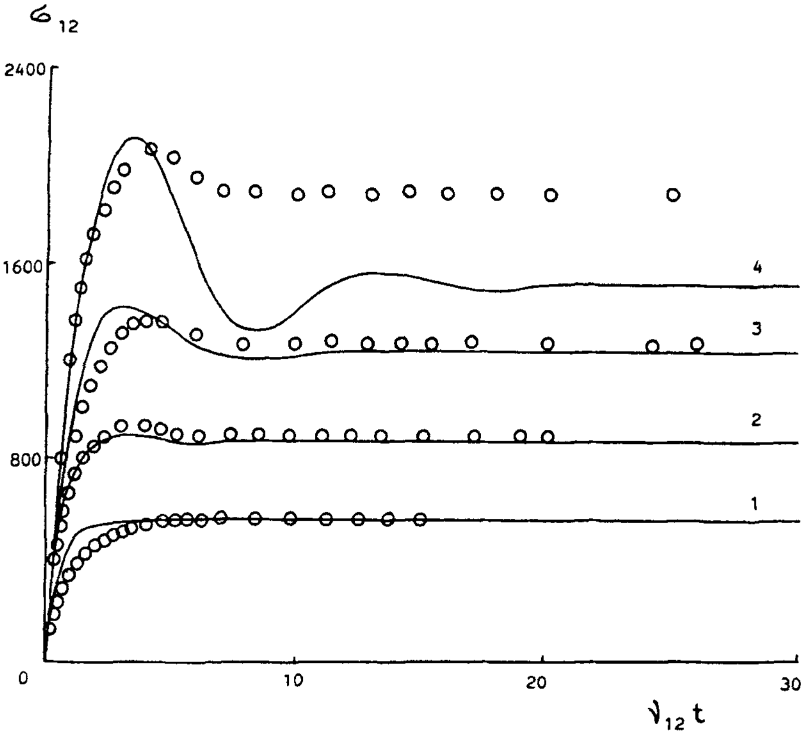

FIGURE 10 Experimental values (dots, according to Trapeznikov, A. and Korotina, T., 1971) and theoretical plot of the shear stress vs. the shear strain (solid lines) for velocity gradients of: 1 – 0.0182; 2 – 0.0313; 3 – 0.0627; 4 – 0.125s^{-1}. The theoretical curves were plotted for values of $nT = 1270$dyn. cm^{-2}; $\eta_0 = 27.5$s; $\chi = 0.11$; $\psi = 12$.

velocity gradients should lead to considerable anisotropy, which in the given example was not considered.

It can be seen from (4.6) that the time dependences of the shear and normal stresses with a steady shear flow (a constant velocity gradient) with a view to the adopted simplifications are monotonic. (Compare with the results in Fig. 5).

5. PULSATING AND OSCILLATING FLOWS IN TUBES

In giving above examples of reducing the determining equations to simpler forms, the authors understood that any simplification is associated with the exclusion of the possibility of analyzing a number of quite fine effects. However, when these effects are secondary or unimportant with respect to the main process, such simplifications are quite justified.

In many specific practical cases, in particular with nonuniform movements of a flowing polymer system in channels having an intricate configuration, it becomes necessary to employ a quite simple system of Equations approximating the flow process in the region of arbitrary velocity gradients. We have already given a system of constitutive Equations (4.2) or (4.3) obtained for the flow of a polymer liquid. When investigating a complex nonuniform flow, it is also convenient to employ system (4.2) or (4.3), setting definite simplifications beforehand. We shall indicate as an example the results of studying the influence of pressure oscillations when a polymer liquid flows in a tube. For this purpose, consider the polymer liquid to flow in a long tube of radius R under the effect of an oscillating pressure difference:

$$p = p_0(1 + A \sin \omega t).$$

5.1. Motion Equations

The basic motion and relaxation equations describing the oscillating and pulsating flows of a viscoelastic fluid (undilute polymer solution) in annular ducts with sinusoidal variations of the pressure gradient in time, as follows from (4.3), are:

$$Re_f \frac{\partial u}{\partial t} = \frac{dp}{dz} + \frac{3}{4} We^{-1} \frac{\partial}{r\partial r}(r\xi_{rz})$$

$$De \frac{\partial \xi_{rz}}{\partial t} = \frac{1}{3} We \frac{\partial u}{\partial r} - \frac{\xi_{rz}}{f(D)}$$

$$De \frac{\partial \xi_{zz}}{\partial t} = 2 We \xi_{rz} \frac{\partial u}{\partial r} - \frac{\xi_{zz} - 1/3}{f(D)} \tag{5.1}$$

$$f(D) = (1 + kD)^{-n}$$

where $dp/dz = (dp/dz)_0(1 + A\sin\omega t)$ and $(dp/dz)_0$ is the steady pressure gradient.

The physical meaning of the criteria is as follows: $Re_f = \rho R^2 \omega/(8\pi\eta_0)$ is the pulsational Reynolds number; $De = \omega\tau_0/(2\pi)$ is the Deborah number; $We = -(dp/dz)_0 R\tau_0/(4\eta_0)$ is the Weissenberg number. When analyzing pulsating flows, the dimensionless elasticity number El equal to the ratio between the Deborah number and pulsational Reynolds number $El = De/Re_f = \eta_0\tau_0/(\rho R^2)$, is frequently used. The set of values of these criteria defines the deviation of the velocity profiles and volumetric flow rates at different phases of the pulsation period from their equilibrium values.

The flow rate characteristics of a pulsating flow of viscoelastic fluids over a wide range of Weissenberg and Deborah numbers and pulsational Reynolds number ($Re_f = 10^{-1} - 0.2$; $We = 0.4 - 5$; $De = 0.01 - 5$) were studied theoretically (Astarita and Marrucci, 1974 and Doi and Edwards, 1986).

We compared calculated results with data for an aqueous polyacrylamide solution. Its rheological properties (the parameter $\kappa = 0.06$, $n = 0.55$, the value of zero-shear-rate viscosity $\eta_0 = 0.323$ Pa·s and the value of $\tau_0 = 1.35$ s in the Equation (5. 1)) were determined by conventional methods of stationary rotational viscosimetry (Astarita and Marrucci, 1974 and Doi and Edwards, 1986).

5.2. Velocity Fields

The frequency of oscillations in the experiments (Altukhov *et al.*, 1986) with the polyacrylamide solution changed in the range of 0.15–0.5 Hz. In this case, the Deborah numbers varied in the range of 0.04–0.13. The pulsating Reynolds number remained small ($Re_f < 10^{-3}$). The oscillating flow of the polyacrylamide solutions is characterized by a pronounced phase shift between the velocity and pressure gradient. The phase shift increased with the frequency and amounted to $\varphi \sim 35\text{–}45^\circ$ under the experimental conditions. In glycerin (Newtonian fluid) flow, the pressure gradient changed by a sinusoidal law, but in a polyacrylamide solution the pressure gradient increased more sharply than it decreased.

A pulsating flow is more complicated than an oscillating one, as the extent of the pressure pulsation effect depends on the value of the steady pressure gradient in the flow (Weissenberg number *We*), which defines the variation rheological properties of the fluid.

In the experiments conducted under inertialess conditions at a constant value of the mean pressure drop ($We = \text{const}$), the frequency f and amplitude A of the pressure gradient variations were changed. In this case, the values of Deborah number were in the same ranges as in oscillating flow, while the amplitude of the oscillations was higher ($A = 0.65\text{–}0.8$).

The values of the axial velocity and changes in velocity over a tube section obtained in experiments were compared with calculations by Equations (5). The results of the calculations for relative velocity values are shown in Figure 11 and Figure 12 by solid lines (the experimental values are shown by dots). One can see from the figures that the calculations describe satisfactorily both the experimentally observed features of the axial velocity changes in different phases of the pulsation period and the velocity profile flatness over the tube section.

5.3. Flow Enhancement

Similar to velocity profiles, the flow rate characteristics of the pulsating flow of a nonlinear viscoelastic fluid depend on their rheological properties and the flow conditions. Measurements were performed with both the sinusoidal and stepwise pressure gradient variation. The change in the flow rate of a pulsating flow in comparison with that of a steady-state one is usually determined by the flow enhancement $I = (Q_p/Q_0) - 1$, where Q_p and Q_0 are the mean flow rates of the pulsating and steady-state flows, respectively. According to the available results of theoretical and experimental studies, the effect of the above criteria on the value of I

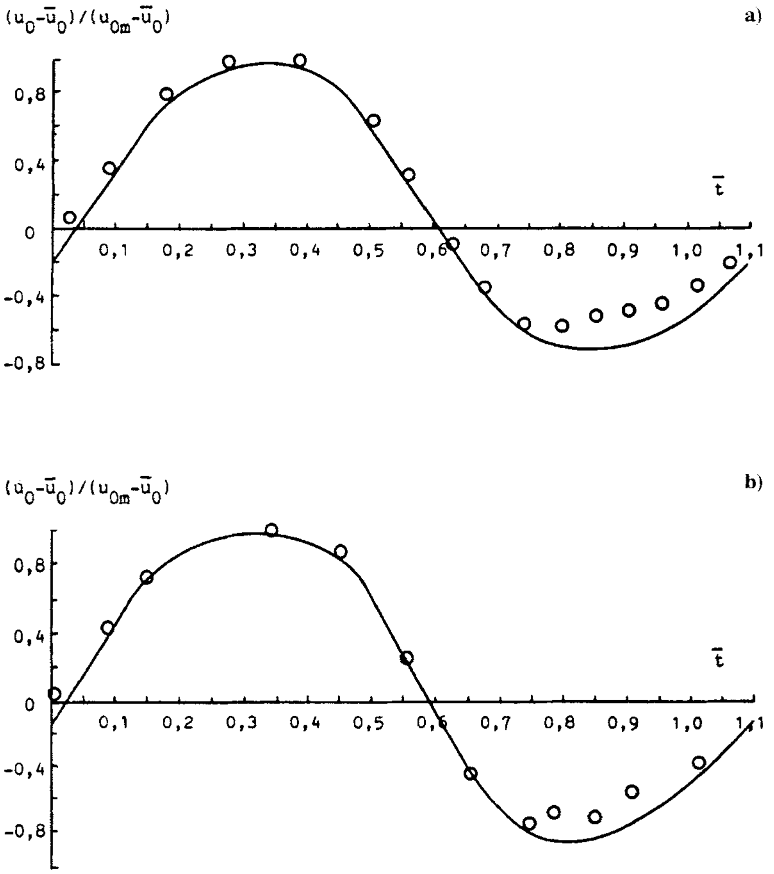

FIGURE 11 Comparison of experimental values (dots) of axial velocity pulsations and calculated ones (solid line). The frequencies of oscillations are: *a* — 0.15 Hz; *b* — 0.5 Hz.

appeared to be different not only qualitatively, but also quantitatively. The system of determining Equations (3–4) was used to study this theoretically.

It had previously been shown theoretically and confirmed experimentally up to values $A \leq 0.45$ the $I \sim A^2$. Our experiments showed that this dependence is valid at substantially higher values of the relative amplitude of the pressure-gradient pulsation. Therefore, in the following, the experimental results will be represented as the basic flow enhancement I/A^2.

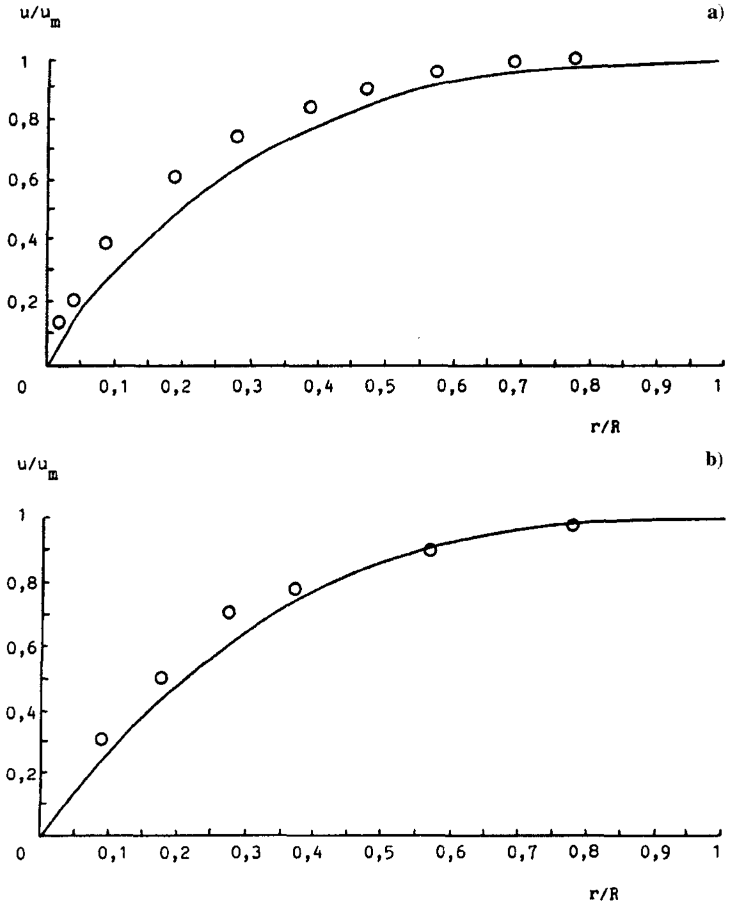

FIGURE 12 Comparison of experimental (dots) and calculated (solid line) velocity profiles. The frequencies of the oscillations are: a — 0.15 Hz; b — 0.5 Hz.

By using aqueous polyacrylamide solutions of different concentrations and changing the pulsation frequency and mean values of the steady pressure gradient, we were able to combine some dimensionless criteria in the experiments.

If $Re_f \gg 1$, the pulsating component of the shear wave does not propagate over the entire tube section during the pulsation period and the pulsation effect on the fluid flow rate will be small.

At $De \ll 1$ one can speak of the equilibrium nature of the flow, when the relaxation properties of the fluid are not practically exhibited. In this case, the pulsation effect will be defined solely by the nonlinear viscous properties of the fluid. This case was considered earlier by a number of authors. One should also not expect a substantial effect of nonlinear viscoelastic properties of fluid at small values of reversible deformations, i.e. at small values of the Weissenberg number.

Case $Re_f \ll 1; De < 1$. Figure 13 shows the experimental and theoretical values of I/A^2 as a function of We for a fixed De. This range of data corresponds to the curve for the theoretically-predicted dependence of I/A^2 on We.

Case $Re_f \ll 1$; $We \approx 4$; $0 < De < 1.2$. Figure 14 presents the values of basic flow enhancement I/A^2 as a function of the Deborah number, obtained for two different values of the Weissenberg number. With an increase in De, the value of I/A^2 decreases at $We = 3.7$, but that of I/A^2 increases weakly at $We = 5.2$.

It was shown theoretically earlier (Altukhov *et al.*, 1986) that the flow enhancement curve I as a function of the dimensionless pulsation frequency had both descending and ascending branches. Previously, experiments could obtain only one branch of the flow enhancement curve $I(De)$, generally, a curve dropping with a growing frequency. In our experiments, for the first time, both branches of the curve of flow enhancement vs. Deborah number were obtained in one experimental setup. The calculations performed for Equations (3–5) confirm this

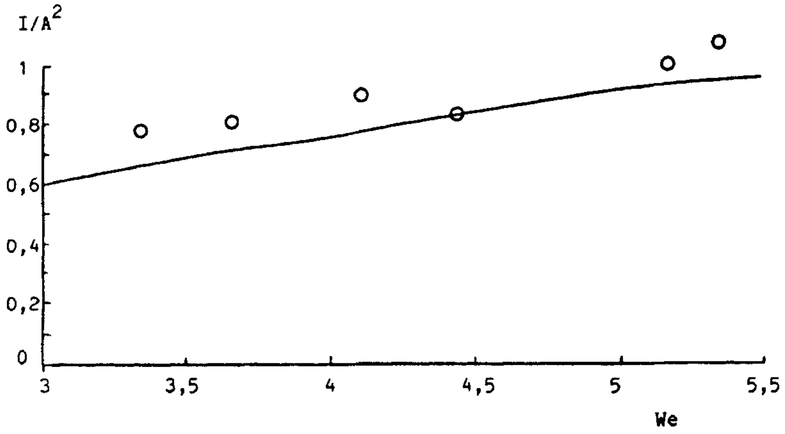

FIGURE 13 Basic low enhancement I/A^2 vs. We for the stepwise law of pressure gradient variation ($De = 0.3$). The dots are experimental values, the solid line- theoretical ones.

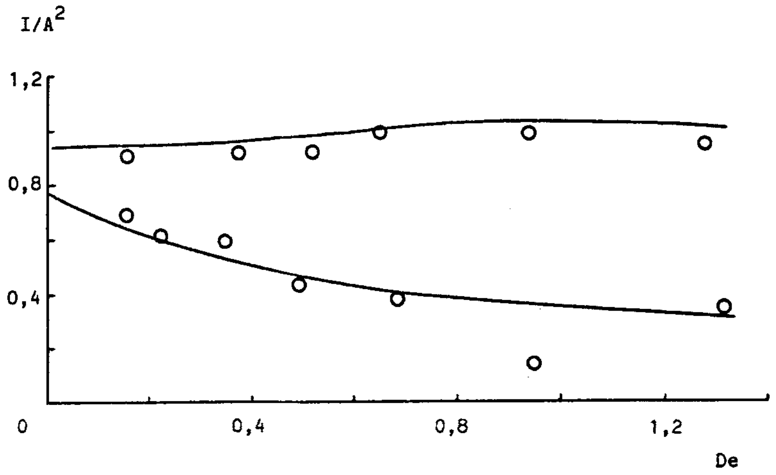

FIGURE 14 Basic flow enhancement I/A^2 vs. *De* for the stepwise law of pressure gradient variation (*We*:1 — 5.2; 2 — 3.7).

result (Fig. 15). Both the regions of decreasing and increasing flow rates with an increasing Deborah number were found.

One can see form the experiments and calculations that at certain combinations of the viscoelastic fluid properties and parameters of pressure gradient pulsations, a considerable increase in the fluid flow rate can be attained as compared with steady flow with the same mean values of the pressure gradient. However, according to calculation (Astarita and Marrucci, 1974 and Edwards, 1982), this can be achieved only by increasing the power necessary for viscoelastic fluid pumping.

5.4. Nonisothermal Flows

The heat transfer in oscillating flows of viscoelastic fluids with sinusoidal variations of the pressure gradient in time are studied theoretically. The system (4), (5) together with energy equation

$$Fo^{-1}\frac{\partial T}{\partial t}+Peu\frac{\partial T}{\partial z}=\frac{\partial^2 T}{\partial r^2}+\frac{\partial^2 T}{\partial z^2}$$

$$r=0,\ \partial u/\partial r=\partial T/\partial r=0;\ r=1,\ u=0,\ T=1;$$

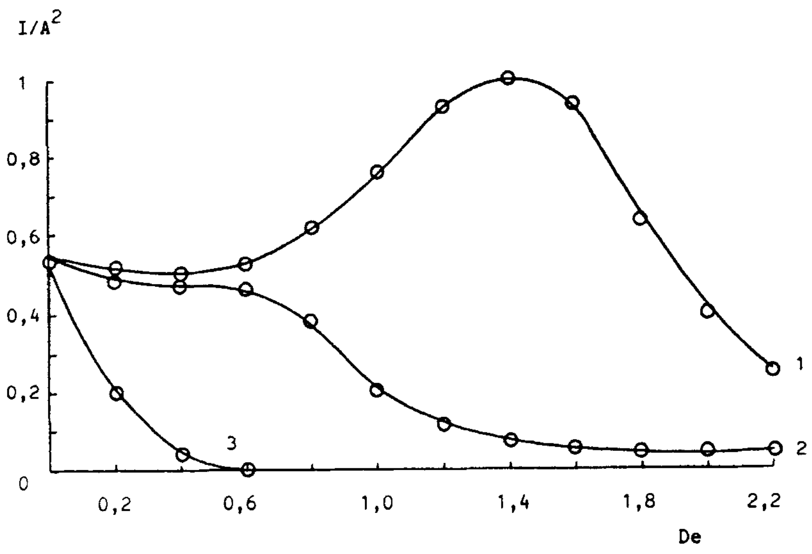

FIGURE 15 Basic flow enhancement I/A^2 vs. De. ($We = 0.28$).

$$x = 0,\ T = 0;\ x \to \pm \infty,\ \partial T/\partial x = 0 \tag{6}$$

where T is a dimensionless temperature; Fo is the Fourier number and Pe is the Pecle number, was used as the basic system to study unsteady-state heat transfer in a round tube (Popov and Altukhov, 1992).

The chief results of the calculations are shown in Figures 16–17. As can be seen from the calculations, a resonance regime of heat transfer may exist in oscillating flows.

Let us note in conclusion that a numerical and experimental studies of the secondary flows that occur in the laminar pressure-driven motion of polymer solutions in ducts of noncircular cross-section were performed. A numerical and experimentally study of the secondary flows that occur in the laminar pressure-driven motion of dilute polymer solutions in ducts of a rectangular cross-section is presented. The full nonlinear two-dimensional equations of motion for a viscoelastic fluid with shear thinning are solved by an explicit finite-difference technique. The results are presented that indicate the existence of the

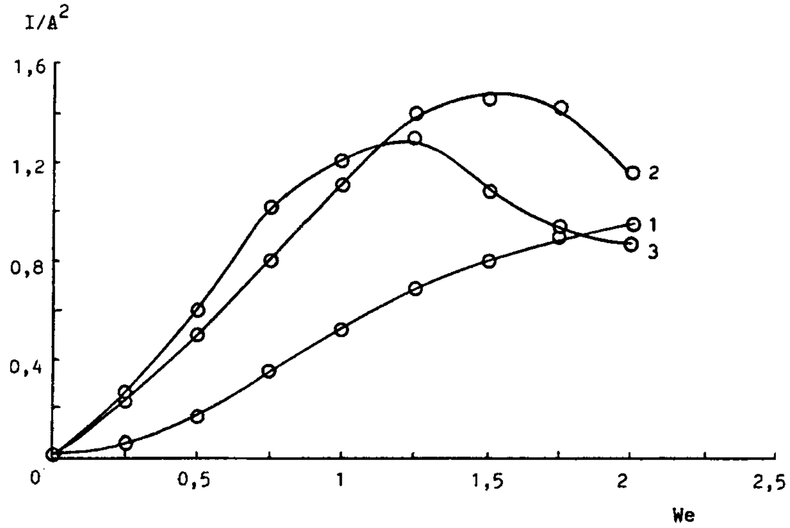

FIGURE 16 Basic flow enhancement I/A^2 vs. We. ($El = 50$).

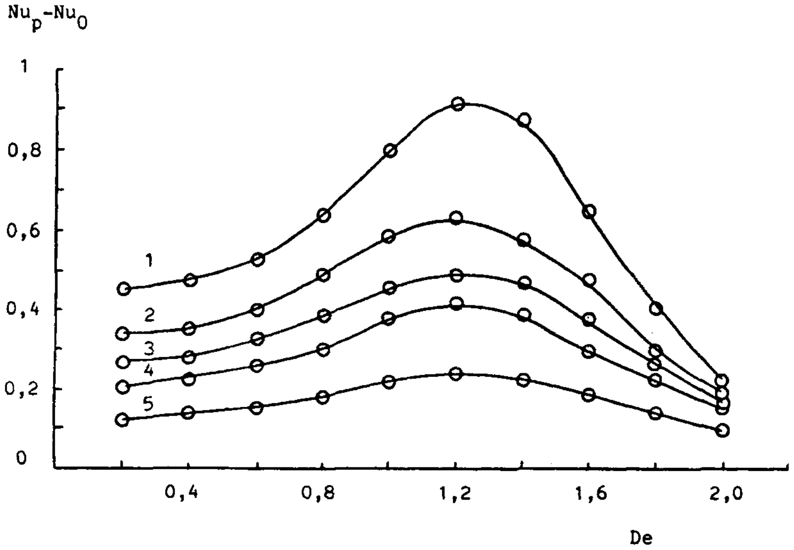

FIGURE 17 The difference of unsteady Nusselt number and steady one vs. De. Curves 1 – 5 are the values of $Pe^{-1}\ x/d$: 1 – 0.128; 2 – 0.266; 3 – 0.5; 4 – 0.675; 5 – 1.9, respectively.

TABLE I *Characteristics of presented systems*

System	*T C*	*c,%*	$\eta_0 \cdot \tau_0$	$\eta_0, Pa.s$	τ_0, s	*N*
High Density Polyethylene [Park, H. J. *et al.*, 1992]	180	100	2.5×10^4	2.8×10^4	1.12×10^0	1
Low Density Polyethylene [Luo, X. L. and Mitsoulis, E., 1990]	160	100	1.45×10^3	5.65×10^4	3.89×10^1	2
Aqueous solution of Polyacrilamide (0.05% w.) [Deiber, J. A. and Schowalter, W. R., 1981]	22	--	9.45×10^0	1.37×10^0	1.45×10^{-1}	3

previously observed vortex secondary flow in ducts of a noncircular cross-section. It was demonstrated experimentally and theoretically that the laminar pressure driven flow of a viscoelastic fluid in noncircular ducts is not unidirectional like its Newtonian counterpart. A weak secondary flow occurs in the transverse planes of the ducts that causes fluid particles to undergo a spiraling motion down the duct in contrast to the rectilinear particle paths in a Newtonian fluid.

6. CONCLUSION

The use of the methods of statistical mechanics to derive rheological equations of state made significant progress in recent years and made possible a unified approach (based on an ideal model) that gives a satisfactory description of the experimental date on the viscoelasticity of polymers in connection with their molecular structure. At any rate the results are useful in understanding the approaches used in the phenomenological theories of polymer dynamics.

We considered the constitutive equations of the theory obtained on the basis of the hypothesis of the dynamics of a macromolecule presuming its motion in an after-effect medium. Subsequently, the hypothesis was discussed in detail in works of Russian investigators. A number of experimental appraisals of the theory undertaken by the authors (Vinogradov *et al.*, 1972, Pokrovskii and Yanovsky 1973, Yanovsky *et al.*, 1988, Yanovsky 1993, Pyshnograi *et al.*, 1994), and also other estimates showed that the considered nature of the thermal motion of a macromolecule is close to the real one. The conclusions of the theory and its results were also extended to nonlinear phenomena. In their corollaries, the conclusions of the theory correspond to the observed experimental results. The determining equations can be formulated in various approximations.

It should be noted that the proposed dynamics of a macromolecule in an undilute system can be used to study behavior of the surface layers. Unlike the previous case, we must add the forces attracting a macromolecule to the surface- nonlinear terms.

We should to use computer simulation methods to analyze the behavior of a macromolecule on the basis of non-linear macromolecular dynamics. These methods allow us to follow the trajectory of a macromolecule and calculate the averaged values under different surface forces.

The investigation of macromolecules gives the mean length of a surface layer. The investigation of the time correlation function gives the set of relaxation times of the macromolecule near the surface.

Consequently, the length of the surface layer and its relaxation times can be calculated from the dynamics of a single macromolecule.

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