separates the region of the primary convective heat transfer $(\mathrm{Pr} > \mathrm{Pr}_*)$, from the region of the primary conductive heat transfer $(\mathrm{Pr} < \mathrm{Pr}_*)$.

Indeed, if the thermal flux at infinity is zero, then $\tau_1 \equiv 0$, and in the case of $\mathrm{Pr} > \mathrm{Pr}_*$ the principal term, as $R \to \infty$, represents the particular solution of the inhomogeneous equation (2): $z(x) R^{-2}$, and the temperature at infinity will be determined by the dissipative heating and not by the heat source on the sphere $R = R_0$. If on the other hand $\mathrm{Pr} < \mathrm{Pr}_*$, then the dipole term of the solution of the homogeneous Eq.(2) will become principal as $R \to \infty$, i.e. in this case the influence of the boundary condition at $R = R_0$ will extend to infinity, the latter effect being characteristic for conductive heat conduction.

If the heat flux at infinity is not zero, then it hardly makes sense to distinguish between those two modes of heat transfer. It should be noted that the possibility of separating the heat transfer modes depends essentially on the manner in which the heat source, which in the present case is the viscous dissipation of kinetic energy of the fluid, is distributed throughout the volume.

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ON THE NON-LINEAR MAXWELL-TYPE DEFINING EQUATIONS FOR DESCRIBING THE MOTIONS OF POLYMER LIQUIDS*

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The problem of using non-linear Maxwell equations containing elastic deformation as the intermediate parameter, to approximate experimental data on the motion of polymer liquids under arbitrary elastic deformations, is studied. The data used concern the simple shear, uniaxial tension and pure shear. The form of the dependence of the free eneryg and rate of irreversible deformation on the elastic deformation is expressed in specific terms. It is assumed that in the course of the deformation, directional phenomena such as crystallization and mechanical destruction play a negligible part. Maxwellian models where the total deformation is separated into the elastic and the irreversible part, were constructed in /1-12/**, initially in the region of small elastic deformations /1-3/. (**See also: Kuvshinskii E.V. Study of the flows of macropolymer solutions (Mechanics of Elastic and Viscoelastic Media). Dis. na soiskanie uch. st. dokt.fiz.matem.nauk. Leningrad, Leningr.fiz.-tkhn.in-t,1950; Leonov A.I. On the description of rheological behaviour of viscoelastic media under large elastic deformations. Preprint In-ta problem mekhan. Akad. Nauk SSSR, Moscow, No.34, 1973; Leonov A.I. Non-equilibrium thermodynamics and rheology of viscoelastic polymer media. Preprint lektsii prochitannoi v Mezhdunarodnoi shkole "Problemy teplo- i massoperenosa v reologicheski slozhnykh sredakh "Minsk, 1975).

The present paper deals with the basic propositions developed in /7, 8,10/ for Maxwell media. Basically, we use the approach of /7/ in which the general form of Maxwell's equations is obtained within the framework of quasilinear non-equilibrium thermodynamics under the assumption that the locally equilibrium state of the medium is non-linearly elastic. The drawbacks apparent in the description of the experimental facts, based on specific equations, are noted and a simple method for overcoming them is proposed.

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1. Separation of the deformation into its reversible (elastic) and irreversible parts. We assume /7,11/ that every deformed state of the viscoelastic medium $\mathbf{x} = \{x^i\}$ described by the Maxwell model can be put in simultaneous 1:1 correspondence with the initial undeformed $\xi = \{\xi^i\}$ state and the unloaded state $\eta = \{\eta^i\}$ in which a small element of the medium arrives when it deforms elastically after the removal of stress. Such an assumption makes it possible /12/* to introduce, together with the total deformation gradient tensor (*See also: Entov V.M. Dynamics of viscous and elastic fluid films. Preprint In-ta problem mekhan. Akad. Nauk SSSR, No.130, Moscow, 1979.) Φ $(dx = \Phi\cdot d\xi)$, the tensors of reversible Φ_e $(dx = \Phi_e\cdot d\eta)$ and irreversible Φ_p $(d\eta = \Phi_p\cdot d\xi)$ deformation. Differentiating these expressions with respect to time t with the Lagrangian coordinates ξ^i fixed, we find that the velocity gradient (a dot denotes a time derivative)

$$\nabla_x \mathbf{v} = \Phi^{\cdot}\cdot\Phi^{-1} = \Phi_e^{\cdot}\cdot\Phi_e^{-1} + \Phi_e\cdot\Phi_p^{\cdot}\cdot\Phi_p^{-1}\cdot\Phi_e^{-1}$$

We define the deformation rate and vorticity tensors as follows:

$$\Phi^{\cdot}\cdot\Phi^{-1} = \mathbf{e} + \omega, \quad \Phi_e^{\cdot}\cdot\Phi_e^{-1} = \mathbf{e}_e + \omega_e$$
$$\Phi_e\cdot\Phi_p^{\cdot}\cdot\Phi_p^{-1}\cdot\Phi_e^{-1} = \mathbf{e}_p + \omega_p$$

and we have for them

$$\mathbf{e} = \mathbf{e}_e + \mathbf{e}_p, \quad \omega = \omega_e + \omega_p \tag{1.1}$$

The total deformation, e.g. the Finger measure $c = \Phi\cdot\Phi^T$ is connected with the tensors $\mathbf{e}, \omega$, by the following relation (see e.g. /7,11/):

$$\mathbf{c}^{\cdot} - \omega\cdot\mathbf{c} + \mathbf{c}\cdot\omega - \mathbf{e}\cdot\mathbf{c} - \mathbf{c}\cdot\mathbf{e} = 0 \tag{1.2}$$

and we have exactly the same relation for the elastic components of the kinematic tensors

$$\mathbf{c}_e^{\cdot} - \omega_e\cdot\mathbf{c}_e + \mathbf{c}_e\cdot\omega_e - \mathbf{e}_e\cdot\mathbf{c}_e - \mathbf{c}_e\cdot\mathbf{e}_e = 0, \quad \mathbf{c}_e = \Phi_e\cdot\Phi_e^T \tag{1.3}$$

The derivation of (1.2) and (1.3) is identical.

In relation (1.3) of /7,8,10/ it was assumed that

$$\omega_e \equiv \omega \tag{1.4}$$

Some arguments supporting this assumption were given in /12/ (one of them is given below).

Using relations (1.1) and (1.4), we shall rewrite relation (1.3) in its final form (the index s denotes the symmetrization operation)

$$\mathbf{c}_e^{\cdot} - \omega\cdot\mathbf{c}_e + \mathbf{c}_e\cdot\omega - 2(\mathbf{e}\cdot\mathbf{c}_e)^s + 2(\mathbf{e}_p\cdot\mathbf{c}_e)^s = 0 \tag{1.5}$$

Relation (1.5) connects the elastic deformation tensors $\mathbf{c}_e$ and irreversible deformation tensor $\mathbf{e}_p$ with the kinematic tensors $\mathbf{e}$ and ω.

In the region of small elastic deformations $\mathbf{c}_e = \delta + \Delta$ (δ is the unit tensor and $\|\Delta\| \ll 1$, the brackets denote the norm of the tensor), relation (1.5) transforms to the well-known form:

$$d\Delta / dt = 2(\mathbf{e} - \mathbf{e}_p) \tag{1.6}$$

Since polymer liquids are usually assumed incompressible, it follows that /7/

$$\det \mathbf{c}_e = 1, \quad \operatorname{tr} \mathbf{e} = \operatorname{tr} \mathbf{e}_p = 0 \tag{1.7}$$

2. Determining the stress in terms of elastic deformation. In the relevant publications it is assumed that the free energy of the medium f is a function of the elastic deformation tensor $\mathbf{c}_e$ and the temperature T. For a Maxwell medium the stress tensor has the form, according to /7,8,10/, analogous to the stress tensor for an elastic isotropic medium /11,13/ (ρ is the density)

$$\sigma = 2\rho\mathbf{c}_e\cdot\partial f/\partial\mathbf{c}_e \quad (\sigma_{ij} = 2\rho c_{e,\,ik}\partial f/dc_{e,\,kj}) \tag{2.1}$$

In using the component-wise notation we have assumed here and below that the Eulerian coordinate system is rectangular and Cartesian.

If the medium is incompressible, we can introduce the elastic potential $W = \rho_0 f$ $(\rho = \rho_0 = \text{const})$. In this case formula (2.1) can be written in the form

$$\sigma = -p\delta + 2\frac{\partial W}{\partial I_1}\mathbf{c}_e - 2\frac{\partial W}{\partial I_2}\mathbf{c}_e^{-1} \tag{2.2}$$

where the multiplier p is found from the boundary conditions, and I_1 and I_2 are invariants appearing in the Hamilton-Cayley equation

$$I_1 = \operatorname{tr}\mathbf{c}_e, \quad I_2 = \operatorname{tr}\mathbf{c}_e^{-1} \; (I_3 = \det\mathbf{c}_e \equiv 1) \tag{2.3}$$

Here by an isotropic elastic medium we mean a medium of the crosslinked rubber type, and this is reflected in the specific form of the elastic potential W (see below).

In the region of small elastic deformations (2.2) becomes Hooke's Law (μ is the modulus of elasticity)

$$\sigma = -p\delta + 2\mu\Delta \tag{2.4}$$

3. Defining the irreversible rate of deformation in terms of elastic deformation.

To close the system of rheological equations (1.5), (1.7) and (2.2), we must specify the form of the isotropic function $\mathbf{e}_p(\mathbf{c}_e)$. Its isotropy follows from the expression describing the dissipation of a weakly non-equilibrium system /7/. In this case, using the conservation laws and the Gibbs expression and assuming that the isotropically elastic state represents the local equilibrium (basic) state we can write, under isothermal conditions, the following expression for the dissipative function in the form

$$D = \sigma : \mathbf{e} - \rho_0 f^{\cdot}|_T = \sigma : \mathbf{e}_p = \sigma^* : \mathbf{e}_p \geqslant 0 \quad (\sigma^* : \mathbf{e}_p = \operatorname{tr} \sigma^* \cdot \mathbf{e}_p) \tag{3.1}$$

where $\mathbf{e}_p$ satisfies (1.5), as was shown in [7]; σ^* is the stress deviator. The final expression for D was also obtained in /8/ by a somewhat different method.

From the assumption of a linear relationship between the forces and energy fluxes ($e_{p,ij} = A_{ijkm}(c_e, T)\,\sigma_{km}^*$) and from (2.2), there follows /7/ the isotropy of the relation $\mathbf{e}_p(\mathbf{c}_e)$. Taking into account the condition of incompressibility, we can write the latter relation, for the general case, in the form

$$\mathbf{e}_p = b_1(I_1, I_2)(\mathbf{c}_e - {}^1/_3 I_1 \delta) - b_2(I_1, I_2)(\mathbf{c}_e^{-1} - {}^1/_3 I_2 \delta) \tag{3.2}$$

where the expressions for I_1 and I_2 are given by (2.3).

In the region of linear viscoelasticity ($c_e \to \delta$) we have

$$\mathbf{e}_p = \Delta/(2\theta), \quad \theta = \eta/(2\mu) \tag{3.3}$$

where η is the viscosity of the system and θ is the relaxation time.

We also note that the antisymmetric tensor ω_p can probably be regarded /12/, by analogy with $\mathbf{e}_p$, as an isotropic function of $\mathbf{c}_e$, and this leads to the relation $\omega_p \equiv 0$ (see (1.1), (1.4)).

Further specification of $b_1(I_1, I_2)$ and $b_2(I_1, I_2)$ in (3.2) is carried out by making assumptions on the basis of arguments of simplicity and correspondence with experimental data.

In /7,10/ it was assumed that, as in the region of linear viscoelasticity, the following relation (see (2.3) and (3.3)) holds in the non-linear domain of medium deformation:

$$\sigma^* = 2\eta \mathbf{e}_p \tag{3.4}$$

In this case

$$b_1 = \frac{1}{\eta}\frac{\partial W}{\partial I_1}, \quad b_2 = \frac{1}{\eta}\frac{\partial W}{\partial I_2}$$

where η can depend, in general, on the invariants of the tensor $\mathbf{c}_e$. A formula similar to (3.4) was also given in /8/.

We note that the system of rheological equations (1.5), (1.7), (2.2), (3.4) obtained characterizes the deformation of metals. In the case of polymers in the viscofluid state it fails to describe a number of simplest experimental facts, e.g. the behaviour of normal stresses in the case of a simple stationary shear (see below).

In /7/, the anisotropy of the viscous properties was taken into account, unlike (3.4), and it was assumed that

$$b_1 = \frac{1}{\eta}\frac{\partial\psi}{\partial I_1}, \quad b_2 = \frac{1}{\eta}\frac{\partial\psi}{\partial I_2}, \quad 2\psi = W(I_1, I_2) + W(I_2, I_1) \tag{3.5}$$

We note that in the case of polymers $W(I_1, I_2)$ is a non-symmetric function of I_1 and I_2 and Eq.(3.4) fails to hold for the case (3.5).

Use of the system of rheological equations (1.5), (1.7), (2.2), (3.2), (3.5), obtained in /7/ made it possible to describe, for the first time, the basic set of non-linear effects arising in the course of the deformation of polymer liquids. The solution of this system for $\eta = \text{const}$ gave, in the case of classical potential of the lattice theory of high elasticity /14/

$$W = \mu(I_1 - 3) \tag{3.6}$$

a good quantitative description (two Maxwell elements connected in parallel were used in the quantitative description) of experimental data concerning the elastic deformations under simple shear and elongation /15,16/*. It was found however, that the description(*see also: Prokunin A.N. Non-linear elastic effects during the stretching of polymer liquids. Experiment and Theory. Preprint In-ta problem mekhan. Akad. Nauk SSSR, No.4, Moscow, 1978.) of the stresses in the cases studied was unsatisfactory at high rates of deformation.

An attempt was made in /9/ to correct the discrepancies shown by introducing a potential of a more general type /17/ (see below), since the domain of applicability of the potential (3.6) is restricted with respect to the deformations /14/. Although the use of the potential

/17/ improved the agreement between the theoretical and experimental relations connecting the tangential stresses and shear deformation rate, it did not minimize the discrepancies arising during stretching.

Below we propose to remove the discrepancies shown, by putting

$$b_1 = b_2 = \mathrm{const} \tag{3.7}$$

with $T = \mathrm{const}$. Then the expression for $\mathbf{e}_p$ (3.2) will, according to (3.3), take the form (θ is the relaxation time)

$$\mathbf{e}_p = (4\theta)^{-1} [(\mathbf{c}_e - {}^1/_3 i_1 \boldsymbol{\delta}) - (\mathbf{c}_e^{-1} - {}^1/_3 I_2 \boldsymbol{\delta}) \tag{3.8}$$

Equations (1.5), (1.7), (2.2), (3.8) with θ independent of $\mathbf{c}_e$, form a closed system of rheological equations, and their advantage is illustrated by the following arguments:

in the case of the elastic potential of the lattice theory of high elasticity (3.6) they are identical with the system of equations /7/ (see (1.5), (1.7), (2.2), (3.2), (3.5)), whose solution in this case yields a good quantitative description of a large number of experiments on shear and elongation /15,16/:

the rheological equations become simpler compared with those given in /7/, and this enables us, in particular, to use easily various elastic potentials in the study of the flows with prescribed kinematics;

when the potential used in (1.5), (1.7), (2.2), (3.8) is of a more general form than (3.6) /17/ (see below), it becomes possible to correct the discrepancies in the solutions of the system noted above in the stress experiment, without changing the theoretical description of the development of the motions and behaviour of elastic deformations with time.

We also note that for every concrete potential W it must be confirmed that the second law of thermodynamics (3.1) is satisfied.

4. Specification of the form of the elastic potential.

It was shown experimentally /18/ that the following two-parameter potential holds for crosslinked rubbers up up to at least approximately tenfold extension:

$$W = (4\mu/n^2)\ \mathrm{tr}\,(\mathbf{c}_e^{n/2} - \boldsymbol{\delta}) \tag{4.1}$$

where μ is the modulus of elasticity and $n > 0$ is a numerical constant. When $n = 2$, the potential (4.1) coincides with the classical potential (3.6).

In the case of the elastic potential (4.1) the expression for the stress has, according to (2.2), the form

$$\boldsymbol{\sigma} = -p\boldsymbol{\delta} + (4\mu/n)\,\mathbf{c}_e^{n/2} \tag{4.2}$$

where the spherical tensor appears as a result of taking into account the condition of incompressibility.

It can be shown that in the case of rheological equations for the fluid in question and potential (4.1), the second law of thermodynamics (the positiveness of the dissipative function $D(\mathbf{c}_e)$ when $\mathbf{c}_e \neq \boldsymbol{\delta}$ holds).

The tensors $\mathbf{c}_e^{n/2}$ and $\mathbf{e}_p(\mathbf{c}_e)$ can be reduced, in this case, by the same coordinate transformation, to the diagonal form

$$\begin{gathered}\bar{\mathbf{c}}_e^{n/2} = \mathrm{diag}\,\{c_{e,1}^{n/2}, c_{e,2}^{n/2}, c_{e,1}^{-n/2} c_{e,2}^{-n/2}\} \\ \mathbf{e}_p = \mathrm{diag}\,\{e_{p,1}, e_{p,2}, -(e_{p,1} + e_{p,2})\}\end{gathered} \tag{4.3}$$

where $c_{e,2} > 0$ and $c_{e,1} > 0$ are the principal independent values of the tensor $\mathbf{c}_e$, taking the conditions of incompressibility (1.7) into account. The expressions connecting the quantities $e_{p,1}$, $e_{p,2}$ and $c_{e,1}$, $c_{e,2}$, have, according to (3.8), the form

$$\begin{gathered}e_{p,1} = (12\theta c_{e,1} c_{e,2})^{-1} (c_{e,1} - 1)\,[c_{e,1} c_{e,2}^2 + 2c_{e,2}(c_{e,1} + 1) + 1] \\ e_{p,2} = (12\theta c_{e,1} c_{e,2})^{-1} (c_{e,2} - 1)\,[c_{e,1}^2 c_{e,2} + 2c_{e,1}(c_{e,2} + 1) + 1]\end{gathered} \tag{4.4}$$

From (4.4) it follows that $e_{p,1} > 0$, $e_{p,2} > 0$ for $c_{e,1} > 1$, $c_{e,2} > 1$ and $e_{p,1} < 0$, $e_{p,2} < 0$ for $c_{e,1} < 1$, $c_{e,2} < 1$.

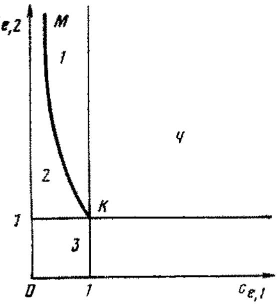

Fig.1

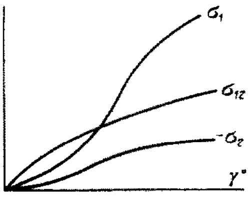

Fig.2

When the stress is given by (4.2), the expression for the dissipative function can be written in terms of the principal axes in the form

$$D = (4\mu/n)\,\mathrm{tr}\,\mathbf{c}_e^{n/2}\cdot\mathbf{e}_p = (4\mu/n)\,[e_{p,1}c_{e,1}^{n/2} + e_{p,2}c_e^{n/2} - (e_{p,1}+e_{p,2})\,c_{e,1}^{-n/2}c_{e,2}^{-n/2}] \tag{4.5}$$

It is clear that for $n > 0$, $D(\mathbf{c}_e) \geqslant 0$ in the domains of values $c_{e,1} \geqslant 1, c_{e,2} \geqslant 1$ and $c_{e,1} \leqslant 1, c_{e,2} \leqslant 1$.

For the final proof of the positiveness of D for any values of $c_{e,1}$ and $c_{e,2}$ we shall show that D takes all its possible values at $c_{e,1} \leqslant 1$, $c_{e,2} \leqslant 1$ (region *3* in Fig.1) and $c_{e,1} \geqslant 1$, $c_{e,2} \geqslant 1$ (region *4*).

Let us now consider the system of variables I_1, I_2

$$I_1 = c_{e,1} + c_{e,2} + (c_{e,1}c_{e,2})^{-1}, \quad I_2 = c_{e,1}^{-1} + c_{e,2}^{-1} + c_{e,1}c_{e,2} \tag{4.6}$$

Since the values of I_1 and I_2 are symmetrical with respect to $c_{e,1}$ and $c_{e,2}$, therefore in what follows it is sufficient to consider the behaviour of $D(I_1, I_2)$ in the region $c_{e,1} < 1$, $c_{e,2} > 1$. The region is divided by the hyperbola $c_{e,2} = c_{e,1}^{-1}$ (see Fig.1, curve *KM*) into two regions, $c_{e,1} < 1, c_{e,2} \geqslant c_{e,1}^{-1}$ (region *1*) and $c_{e,1} < 1, c_{e,2} \leqslant c_{e,1}^{-1}$ (region *2*). It can be confirmed (see (4.6)) that for any point of the region *1* $c_{e,1} = t$, $c_{e,2} = t^{-n}$ $(n \geqslant 1, 0 < t < 1)$ we can find a point of the region *3* $c_{e,1} = t, c_{e,2} = t^{n-1}$ for which I_1 and I_2 will be the same. Similarly we can find for any point of the region *2* $c_{e,1} = t$, $c_{e,2} = t^{-n}$ $(0 < n \leqslant 1, 0 < t < 1)$, a point of the region *4* $c_{e,1} = t^{-n}$, $c_{e,2} = t^{n-1}$. Thus all possible values of the function $D(I_1, I_2) = D_*(c_{e,1}, c_{e,2})$ are realized in the regions *3* and *4*, and $D(\mathbf{c}_e) > 0$ when $\mathbf{c}_e \neq \boldsymbol{\delta}$.

5. Comparison of the theoretical and experimental results.

Next we shall use the proposed version to study the Maxwell model of simple and pure shears, and of uniaxial elongation. The results of the corresponding experiments with a solution of butyl rubber in transformer oil and with a polyisobutylene melt can be found in e.g. /15,16/*. The first (* see also: Prokunin A.N. Non-linear elastic effects during the stretching of polymer liquids. Experiment and Theory. Preprint In-ta problem mekhan. Akad. Nauk SSSR, No.4, Moscow, 1978.) preliminary experiments on pure shear were carried out for polyisobutylene in /18/.

Simple shear ususally takes place between two plates one of which is fixed and the other of which moves parallel to the first in direction *1*. The axis *2* is perpendicular to the plates. In this case the kinematic matrices have the form

$$\mathbf{e} = \frac{\gamma^{\cdot}}{2}\begin{Vmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{Vmatrix}, \quad \boldsymbol{\omega} = \frac{\gamma^{\cdot}}{2}\begin{Vmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{Vmatrix} \tag{5.1}$$

$$\mathbf{c}_e = \begin{Vmatrix} c_{e.11} & c_{e.12} & 0 \\ c_{e.12} & c_{e.22} & 0 \\ 0 & 0 & 1 \end{Vmatrix}$$

where $\gamma^{\cdot} > 0$ is the rate of deformation depending, in general, on time.

The matrix $\mathbf{c}_e$ is reduced by an orthogonal transformation to its diagonal form

$$\mathbf{c}_e{}^* = \mathrm{diag}\,\{c_e, c_e^{-1}, 1\} = \mathbf{q}^{-1}\cdot\mathbf{c}_e\cdot\mathbf{q} \tag{5.2}$$

$$\mathbf{q} = \begin{Vmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{Vmatrix}$$

where the condition of incompressibility (1.7) was taken into account when writing the expression for $\mathbf{c}_e{}^*$ in (5.2). Substituting the matrices (5.1) into (1.5), (3.8) taking (5.2) and the conditions of incompressibility of the medium into account, we obtain

$$\begin{aligned}
&c_{e,11}^{\cdot} + (4\theta)^{-1}(c_e - c_e^{-1})\,[c_e - c_e^{-1} + (c_e + c_e^{-1})\cos 2\varphi] = 2\gamma^{\cdot}c_{e,12} \\
&c_{e,12}^{\cdot} + (4\theta)^{-1}(c_e - c_e^{-1})(c_e + c_e^{-1})\sin 2\varphi = \gamma^{\cdot}c_{e,22} \\
&2c_{e,11} = c_e + c_e^{-1} + (c_e - c_e^{-1})\cos\varphi \\
&2c_{e,22} = c_e + c_e^{-1} - (c_e - c_e^{-1})\cos\varphi \\
&2c_{e,12} = (c_e - c_e^{-1})\sin 2\varphi
\end{aligned} \tag{5.3}$$

System (5.3) yields the relations $c_e(t)$ and $\varphi(t)$.

Remembering that $\mathbf{c}_e^{n/2} = \mathbf{q}\cdot\mathbf{c}_e^{*n/2}\cdot\mathbf{q}^{-1}$, we can obtain expressions for the stress tensor components (4.2) in terms of c_e and φ.

The following quantities are usually measured in experiments with polymer liquids:

$$\begin{aligned}
&\sigma_1 = \sigma_{11} - \sigma_{22} = 4\,(\mu/n)\,(c_e^{n/2} - c_e^{-n/2})\cos 2\varphi \\
&\sigma_2 = \sigma_{22} - \sigma_{33} = 2\,(\mu/n)\,[c_e^{n/2} + c_e^{-n/2} - 2 - (c_e^{n/2} - c_e^{-n/2})\cos 2\varphi]
\end{aligned} \tag{5.4}$$

$$\sigma_{12} = 2\,(\mu/n)\,(c_e^{n/2} - c_e^{-n/2}) \sin 2\varphi$$

In the case of stationary flow (5.3) with $\gamma^{\cdot} = \text{const}$), we have

$$\cos 2\varphi = \frac{c_e - c_e^{-1}}{c_e + c_e^{-1}}, \quad \sin \varphi = \frac{2}{c_e + c_e^{-1}}, \quad (c_e + c_e^{-1})(c_e - c_e^{-1}) = 4\theta\gamma^{\cdot} \tag{5.5}$$

and (5.4) become

$$\begin{aligned} \sigma_{12} &= 4\,(\mu/n)\,(c_e^{n/2} - c_e^{-n/2})\,(c_e + c_e^{-1})^{-1} \\ \sigma_1 &= \sigma_{12}\,(c_e - c_e^{-1}) \\ \sigma_2 &= 2\,(\mu/n)\,[c_e^{n/2} + c_e^{-n/2} - 2 - \sigma_1 n/(4\mu)] \end{aligned} \tag{5.6}$$

Figure 2 shows the experimental quantitative dependence of σ_{12}, σ_1 and σ_2 on $\gamma^{\cdot}$. We also note that the dependence of the effective viscosity $\sigma_{12}/\gamma^{\cdot}$ on $\gamma^{\cdot}$ is a monotonically decreasing function and condition $|\sigma_2| \ll \sigma_1$ holds for the normal stresses.

To make a comparison with experiment, we shall consider the asymptotic dependence of σ_1, σ_2 and σ_{12} on the dimensionless parameter $\Gamma = \gamma^{\cdot}\theta$

$$\begin{aligned} &\Gamma \ll 1:\ \sigma_{12} = \eta\gamma + O\,(\Gamma^3), \quad \sigma_1 = 4\mu\theta^2\gamma^{\cdot 2} + O\,(\Gamma^4) \\ &\sigma_2 = -2\mu\theta^2\gamma^{\cdot 2}\,(1 - n/4) + O\,(\Gamma^4), \quad \eta = 2\mu\theta \end{aligned} \tag{5.7}$$

$$\begin{aligned} &\Gamma \gg 1:\ \sigma_{12} \approx 2\,(\mu/n)\,(4\Gamma)^{n-2/4}, \quad \sigma_1 \approx 4\,(\mu/n)\,\Gamma^{n/4} \\ &\sigma_2 = 4\,(\mu/n)\,[1 - (4\Gamma)^{-n/4} - (4\Gamma)^{n-4/4}]; \end{aligned} \tag{5.8}$$

To match this with the experiment, we put

$$4 \geqslant n \geqslant 2 \tag{5.9}$$

When $n < 2$, the relationship $\sigma_{12}(\Gamma)$ passes through a maximum. The descending branch is in this case unstable.

When the direction of motion of the plate is reversed, the rate of deformation changes its sign. In this case from (5.5) it follows that $c_e(-\gamma^{\cdot}) = c_e^{-1}(\gamma^{\cdot})$. Then the stress components σ_1 and σ_2 remain unchanged and the tangential component σ_{12} changes its sign (see (5.4)) When $\Gamma < 0$, the asymptotic formulas for $(-\Gamma) \ll 1$ are analogous to (5.7). When $(-\Gamma) \gg 1$, Γ and σ_{12} in (5.8) should be replaced by $(-\Gamma)$ and $(-\sigma_{12})$.

Homogeneous uniaxial elongation. This usually occurs when stretching a cylinder of polymer liquid. This type of deformation is described, in a fixed Cartesian coordinate system, by the matrices ($\varkappa > 0$ is the rate of deformation)

$$\mathbf{e} = \varkappa \operatorname{diag}\{1, -1/2, -1/2\}, \ \boldsymbol{\omega} \equiv 0, \ \mathbf{c}_e = \operatorname{diag}\{\lambda^2, \lambda^{-1}, \lambda^{-1}\} \tag{5.10}$$

In the expressions for the tensors $\mathbf{e}$ and $\mathbf{c}_e$ the condition of incompressibility of the medium (1.7) was taken into account. Substituting the matrices (5.10) into the equations (1.5), (3.8), (4.2), we obtain the following system of defining equations for the elongation:

$$\frac{\theta}{\lambda}\frac{d\lambda}{dt} + \frac{(\lambda+1)(\lambda^3-1)}{6\lambda^2} = \varkappa\theta, \quad \sigma = \frac{4\mu}{n}(\lambda^n - \lambda^{-n/2}) \tag{5.11}$$

where σ are tensile stresses. In deriving the second formula of (5.11) it was assumed that the stress vanishes at the free surface of the stretched cylinder.

The experiments * carried out on a plyisobutylene melt have shown that in the case (*see also: Prokunin A.N. Non-linear elastic effects during the stretching of polymer liquids. Experiment and Theory. Preprint In-ta problem mekhan. Akad. Nauk SSSR, No.4, Moscow, 1978.) of a stationary flow ($\varkappa = \text{const}$) the stress σ and viscosity $\sigma/\varkappa$ increase monotonically as $\varkappa$ increases. To compare these experimental data, we shall consider the asymptotic behaviour of σ relative to the magnitude of the dimensionless parameter $\Gamma = \varkappa\theta$

$$\Gamma \ll 1:\ \sigma = 3\eta\varkappa + O\,(\Gamma^2); \ \Gamma \gg 1:\ \sigma \approx 4\,(\mu/n)(6\Gamma)^{n/2} \tag{5.12}$$

Formulas (5.12) agree with the experimental data shown when $n > 2$. We note than when $n = 2$ the viscosity increases from 3η to 6η. When $n > 2$ the viscosity increases without limit, and this leads to a more accurate description of the experiment than when $n = 2$.

Pure shear occurs e.g. when a film is stretched in direction 1, without deformation in direction 2 perpendicular to 1. The ends of the film are fixed in this direction, and the surfaces perpendicular to direction 3 are free. In this case we have ($\varkappa > 0$ is the rate of deformation)

$$\mathbf{e} = \varkappa \operatorname{diag}\{1, 0, -1\}, \ \boldsymbol{\omega} \equiv 0, \ \mathbf{c}_e = \operatorname{diag}\{c_e, 1, c_e^{-1}\} \tag{5.13}$$

Subsituting the matrices (5.13) into (1.5), (3.8), (4.2), we obtain a system of rheological equations describing pure shear

$$\frac{\theta}{c_e}\frac{dc_e}{dt}+\frac{c_e{}^2-1}{2c_e}=2\varkappa\theta \tag{5.14}$$

$$\sigma_{11}=4\,(\mu/n)(c_e^{n/2}-c_e^{-n/2}),\quad \sigma_{22}=4\,(\mu/n)(1-c_e^{-n/2})$$

In deriving the expressions for σ_{11} and σ_{22} in (5.14), the fact that $\sigma_{33}\equiv 0$ at the free surface of the medium was taken into account.

Preliminary experiments carried out for $\varkappa=\mathrm{const}$ on polyisobutyline in /18/ have shown that σ_{11} and σ_{22} increase as $\varkappa$ increases when the flow is stationary. The effective viscosity $\sigma_{11}/\varkappa$ is approximately constant within the interval $\varkappa$ in question, and the ratio $\sigma_{22}/\varkappa$ decreases rapidly as $\varkappa$ increases.

In the case of a stationary flow ($\varkappa=\mathrm{const}$ in every experiment), Eqs.(5.14) show that the relation connecting the elastic deformation c_e with the dimensionless parameter $\Gamma=\varkappa\theta$, has the form

$$c_e=2\Gamma+\sqrt{1+4\Gamma^2} \tag{5.15}$$

From (5.14) and (5.15) it follows that

$$\Gamma\ll 1:\ \sigma_{11}=4\eta\varkappa+O\,(\Gamma^3),\quad \sigma_{22}=2\eta\varkappa+O\,(\Gamma^2) \tag{5.16}$$

$$\Gamma\gg 1:\ \sigma_{11}\approx 4\,(\mu/n)(4\Gamma)^{n/2},\quad \sigma_{22}=4\,(\mu/n)[1-(4\Gamma)^{-n/2}] \tag{5.17}$$

Thus the theory agrees with experiment when $n\geqslant 2$ /18/.

Let us consider the case when $\varkappa=\mathrm{const}<0\ (\Gamma<0)$ in the kinetic matrices (5.10) and (5.13). This corresponds to compression of a cylindrical sample or of a film with the edges clamped along the axis 1. When $|\Gamma|\ll 1$, the asymptotic formulas (5.12) and (5.16) remain the same as in the case when $1\gg\Gamma>0$. When $|\Gamma|\to\infty$, the elastic deformation $\lambda\to 0$ in the problems in question. In the case of uniaxial compression we have for $|\Gamma|\gg 1$

$$\sigma\approx -4\,(\mu/n)\,(-6\Gamma)^{n/4}$$

Since $0<n<4$, it follows that for uniaxial stationary compression the effective viscosity diminishes beginning from the value 3η (see (5.12)). When a film with clamped edges is deforrmed we have, for $\Gamma<0$ and $|\Gamma|\gg 1$,

$$\sigma_{11}=\sigma_{22}=-4\,(\mu/n)\,(-4\Gamma)^{n/2}$$

We also note that the experimental realization of these two types of deformation, and especially of the film, is very difficult since the form of the samples is not stable and the inhomogeneities present in the clamped areas affect the deformation.

In the light of what was said above, we can conclude hat a class of polymers exists whose non-linear behaviour in a viscoliquid state is described, over a wide class of deformations, by a Maxwell model with the relaxation time independent of the elastic deformation.

Experiments /19/ carried out on a melt of crystallisable polymer (low density polyethylene) show that its behaviour under tension differs essentially from that predicted by the model with the relaxation time independent of elastic deformations. For example, a retardation of the flow was observed in the polymer. During the deformation stage the polymer lost fluidity, but later the development of the flow followed the behaviour of the plastic media.

To describe the loss of fluidity in the polymer the relaxation time θ was specified in /7/ as an exponentially increasing function of the elastic potential. A qualitative description of the flow retardation can be found in [20, 21]. We note that in /21/a tensor was introduced, taking into account the orientation of the segments forming the macromolecules, in addition to the elastic deformation tensor, to characterize the strain orientation of the macromolecules. A scalar parameter characterizing the concentration of the oriented polymer /22/ may also be found useful in describing the effect of flow retardation.

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