A DESCRIPTION OF THE MOTION OF VISCOELASTIC POLYMER MEDIA

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Governing and temperature equations are presented for polydisperse polymers in a viscous flowing state. The influence of a large relaxation time with a small weight on the motion is clarified.

1. GOVERNING EQUATIONS

A theory of viscoelastic media with intermediate elastic strain parameter is developed in [1]. In particular, a general theory of Maxwellian media is developed in [1, 2] with a number of its specifications for polymers. An improved modification of a Maxwell medium is proposed in [3] in application to melts and concentrated solutions of polydisperse polymers

$$\dot{\mathbf{c}}_k - \omega\cdot\mathbf{c}_k + \mathbf{c}_k\cdot\omega - 2\,(\mathbf{e}\cdot\mathbf{c}_k)^S + 2\,(\mathbf{e}_{p,k}\cdot\mathbf{c}_k)^S = 0, \tag{1}$$

$$\det\mathbf{c}_k = 1,\ \operatorname{tr}\mathbf{e} = 0, \tag{2}$$

$$\boldsymbol{\sigma}_k = (4\mu_k/n_k)\,\mathbf{c}_k^{\frac{n_k}{2}}, \tag{3}$$

$$\mathbf{e}_{p,k} = (4\theta_k^*)^{-1}\left[\left(\mathbf{c}_k - \frac{1}{3}\,I_{1,k}\mathbf{E}\right) - \left(\mathbf{c}_k^{-1} - \frac{1}{3}\,I_{2,k}\mathbf{E}\right)\right], \tag{4}$$

$$I_{1,k} = \operatorname{tr}\mathbf{c}_k,\ I_{2,k} = \operatorname{tr}\mathbf{c}_k^{-1}.$$

The subscript k here denotes belonging to the k-th Maxwell element (relaxation mechanism), the dot denotes the derivative with respect to time, and the letter S the symmetrization operation.

Equations (1) and (4) connect the internal parameter of the medium, the elastic strain tensor $\mathbf{c}_k$ with the external characteristics of the motion, the strain rate $\mathbf{e}$ and vortex $\boldsymbol{\omega}$ tensors. Condition (2) is the condition of incompressibility of the medium. Formula (3) yields a dependence of the stress σ_k (to the accuracy of the pressure) on the elastic strain $\mathbf{c}_k$. It is obtained [2] from an expression for the stress analogous to vulcanized rubber

$$\boldsymbol{\sigma}_k = \rho\,\frac{\partial f_k}{\partial\mathbf{H}_k},\ \mathbf{c}_k = \exp 2\mathbf{H}_k, \tag{5}$$

for the elastic potential [4]

$$W_k = \rho\tilde{f}_k = \left(\frac{4\mu_k}{n_k^2}\right)\operatorname{tr}\left(\mathbf{c}_k^{\frac{n_k}{2}} - \mathbf{E}\right), \tag{6}$$

where $\tilde{f}$ is the free energy to the accuracy of a component dependent on the temperature, the modulus $\mu_k \sim \rho T$ (see (3)) is assumed independent of the temperature for specific computations, and the constant n_k is independent of the temperature.

Equation (4) connects the irreversible strain rate $\mathbf{e}_{p,k}$ to the elastic strain $\mathbf{c}_k$. Distortion of the potential barriers by the stress which we take into account by the following dependence of the relaxation time on the elastic energy:*

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*Mechanical destruction will exert analogous influence on the relaxation time also.

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$$\theta_k^* = \theta_{0,k} \exp\left(\frac{E_k - \gamma_k W_k}{RT}\right) = \theta_k \exp(-m_k W_k),$$

$$m_k = \frac{\gamma_k}{RT}, \ m_k W_k \ll \frac{E_k}{RT}, \tag{7}$$

where the constant γk and the ratio $\gamma_k W_k/RT$ are independent of the temperature, can indeed turn out to be substantial during motion of a polymer medium.

To describe polymer motion in a viscous flowing state N Maxwell elements connected in parallel are combined (under the assumption of a strong difference in the scales of the structural elements of the polymer) [2]. Then the total stress in the system is

$$\sigma = -PE + \sum_{k=1}^{N} \sigma_k, \tag{8}$$

where the scalar p is determined from the boundary conditions. The tensor of the total strain rate **e** is identical in each Maxwell element. It is also assumed [5] that for the system free energy

$$f = \sum_{k=1}^{N} f_k \tag{9}$$

for an identical temperature T in each k-th Maxwell element. Therefore, the system free energy f is a function of T and the elastic strains $\mathbf{c}_k$ (k = 1, ..., N). From assumptions [1, 6] about the local equilibrium of a viscoelastic system

$$T = \frac{\partial u_k}{\partial s_k}, \ s_k = -\frac{\partial f_k}{\partial T}, \tag{10}$$

$$f_k = u_k - Ts_k, \tag{11}$$

from which there follows for the entropy and internal energy of the system

$$s = \sum_{k=1}^{N} s_k, \ u = \sum_{k=1}^{N} u_k. \tag{12}$$

Then, as for each Maxwell element also, for the whole system

$$T = \left.\frac{\partial u}{\partial s}\right|_{\mathbf{c}_1,\ldots,\mathbf{c}_N}.$$

To describe experimental data it is usually sufficient to set N = 2-3 (see [7]). Taking account of a large number of relaxation mechanisms essential for intensive effects (see (2)) is not needed, as a rule, for practical purposes. This is associated with the fact that under intensive action on a medium such phenomena set in as instability of the motion, dissipative heating, separation from the walls, and rupture of the medium.

2. CONSTANTS OF THE MODEL

Each Maxwell element contains four positive constants. Two of them, the relaxation time θ_k and the elastic modulus μk, can be determined in the domain of linear behavior of the medium, where (1)-(7) take the form

$$\theta_k \frac{d\Delta_k}{dt} + \Delta_k = 2\eta_k \mathbf{e}, \tag{13}$$

$$\sigma = -PE + 2\sum_k \mu_k \Delta_k. \tag{14}$$

Here $\mathbf{c}_k = \mathbf{E} + \Delta_k$, $\eta_k = 2\mu_k\theta_k$.

The constants θ_k and μ_k are found [2, 7] from tests on low-amplitude shear vibrations, simple shear with a constant strain rate, or by stress relaxation. Only sufficiently rough agreements of the computational dependences obtained from (13) and (14), with the experimental are achieved here since the assumption of strong diversity in the scales of the relaxation elements is apparently also rough. This latter description of the experiments in the nonlinear domain is usually better than in the linear domain.

The inequalities

$$\theta_1 \gg \theta_2 \gg \theta_3, \tag{15}$$

$$\mu_1 \ll \mu_2 \ll \mu_3, \tag{16}$$

$$\eta_1\theta_1 \gg \eta_2\theta_2 \gg \eta_3\theta_3 \tag{17}$$

are satisfied for these constants in the domain of comparison with experiment* [2, 7].

For a limited intensity of the action on the medium, the third mechanism cannot be taken into account by virtue of (16) because the elastic strains therein are small. Then (8) takes the form

$$\sigma = -P\mathrm{E} + \sum_{k=1}^{2} \sigma_k + s_* \eta \mathrm{e}, \tag{18}$$

where $0 \leqslant s_* \leqslant 1,\ s_*\eta = \eta_3$.

The constants n_k and γ_k are determined in the nonlinear strain domain of the medium. There follows from a qualitative comparison of the theoretical data with experiment (see [2, 3])

$$4 \geqslant n_k \geqslant 2. \tag{19}$$

Usually n_k is assumed independent of k ($n_k = n$). The same must also be said about the energy of viscous flow activation E_k ($E_k = E$), since the principle of temperature—time superposition [8] should be satisfied for polymers in the viscous flowing state. The exception might be a coarse-scale mechanism with small weight (see (5)) for which $n_1 \neq n$ and $E_1 \neq E$ are possible (see [9], Fig. 3).

The constants are $\gamma_k \sim 10^4$–10^5 cm³/mole, which is estimated from the number of molecules per segment [10] taking part in the skipping act. This mechanism is often barely essential ($m_k W_k \ll 1$).

3. EQUATIONS FOR THE TEMPERATURE OF THE MEDIUM

In the general case of a simple liquid, the equation for the temperature of the medium was obtained in [11] for the case of entropy elasticity in the system. As for cross-linked rubber (see [12], say) it is assumed in [1, 6, 11] that the free energy $f = u - TS$ varies for T = const mainly because of a change in the macromolecule configuration (the entropy s). The monomer links themselves, that comprise the macromolecules, are weakly deformed, which results in constancy of the internal energy for an isothermal process. In the case of an assumption about the system entropy elasticity, the equation for the temperature of a viscoelastic medium is analogous to the corresponding equation for ordinary liquids. The correctness of this is confirmed in [11] and experimentally in a polyisobutylene melt under simple shear and tension. Since the model being discussed in [1, 3] is a particular case of a simple liquid, then the temperature equation is valid for it [11]. We duplicate its derivation for our particular case. The first law of thermodynamics in local form and under the assumption of satisfaction of the Fourier heat conduction relationships appears as follows:

$$\rho \frac{du}{dt} = \tilde{\varkappa} \nabla^2 T + \sigma : \mathrm{e}. \tag{20}$$

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*The maximal number of Maxwell elements in [2] was three.

The specific heat under constant elastic strains c_k is

$$c = T\frac{\partial s}{\partial T}\Big|_{\mathbf{c}_1,\ldots,\mathbf{c}_N} = \frac{du}{dT}. \tag{21}$$

The second equality in (21) follows from the relationships (10) and (11). Since u is a function of only the temperature T then the specific heat c is also a function of only the temperature of the medium (see (20) and (21)) and has the form

$$\rho c\frac{dT}{dt} = \tilde{\varkappa}\nabla^2 T + \sigma : \mathbf{e}. \tag{22}$$

The equation for the temperature of the medium (22) can also be obtained from the second law of thermodynamics in local form [6] by substituting an expression there for the entropy production [1]. It is convenient to measure the specific heat c in an unrelaxing medium where c(T) = dQ/dT.

Let us trace how the assumption being used about the entropy elasticity is reflected in the rheological equations (1)-(8). The following representation for the entropy of the medium is found from (21)

$$\begin{gathered} s(T, \mathbf{c}_1, \ldots, \mathbf{c}_N) = \bar{s}(T) + \tilde{s}(\mathbf{c}_1, \ldots, \mathbf{c}_N), \\ s_k(T, \mathbf{c}_k) = \bar{s}_k(T) + \tilde{s}_k(\mathbf{c}_k). \end{gathered} \tag{23}$$

Using (23) as well as the expressions (5) and (6) for the stresses and the free energy (11), we find that the elastic modulus, as for cross-linked rubbers [6, 12], is $\mu_k \sim \rho T$ and that ($\mathbf{c}_k = \exp 2\mathbf{H}_k$)

$$\sigma_k = -\rho T\frac{d\tilde{s}_k}{d\mathbf{H}_k}\Big|_T = -\rho T\frac{\partial s}{\partial \mathbf{H}_k}\Big|_T. \tag{24}$$

Formula (24) shows that the change in the elastic deformation (see (3)) is associated just with the change in entropy in an isothermal process.

Let us still note that (see (22))

$$\sigma : \mathbf{e} = \sum_{k=1}^{N} \sigma_k : \mathbf{e} = \sum_{k=1}^{N}\left(\sigma_k : \mathbf{e}_{p,k} + \sigma_k : \frac{d\mathbf{H}_k}{dt}\right), \tag{25}$$

i.e., the convolution σ:**e** takes account of the change in temperature in the system because of both dissipative heating which occurs for flows and the change in entropy s [6] during elastic strain (see (24)). The expression (25) is obtained from the relation (1) when it is multiplied by $\mathbf{c}^{-1}/2$ and subsequently convoluted with the tensor σ_k (see [1]).

Systems exist (for instance, metals) in which the free energy changes because of the internal energy, i.e.,

$$\frac{\partial s}{\partial \mathbf{H}_k}\Big|_T = 0 \quad (k = 1, 2, \ldots, N).$$

As (25) shows, this naturally results in no entropy heating effect in the system. In the case of flow existence in such systems

$$\rho c\frac{dT}{dt} = \tilde{\varkappa}\cdot\nabla^2 T + \sum_{k=1}^{N} \sigma_k : \mathbf{e}_{p,k}.$$

4. SIMPLE SHEAR AND UNIAXIAL TENSION MOTION

Simple shear is usually realized between two plates, one of which is fixed while the other is displaced parallel to the first in the direction 1. The axis 2 is here directed perpendicularly to the plates. In this case the kinematic matrices have the form

$$\mathbf{e} = \frac{\gamma}{2}\begin{Vmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{Vmatrix}, \quad \omega = \frac{\gamma}{2}\begin{Vmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{Vmatrix}, \quad \mathbf{c}_k = \begin{Vmatrix} c_{k,11} & c_{k,12} & 0 \\ c_{k,12} & c_{k,22} & 0 \\ 0 & 0 & 1 \end{Vmatrix}, \tag{26}$$

where $\gamma \geq 0$ is the shear velocity, independent of the time in the general case.

The matrix c_k is reduced by the orthogonal transformation q_k to the diagonal form†

$$c_k^* = \operatorname{diag}\{c_k,\ c_k^{-1},\ 1\} = q_k^{-1} \cdot c_k \cdot q_k,$$

$$q_k = \begin{Vmatrix} \cos\varphi_k & -\sin\varphi_k & 0 \\ \sin\varphi_k & \cos\varphi_k & 0 \\ 0 & 0 & 1 \end{Vmatrix}, \tag{27}$$

where the incompressibility condition (2) was taken into account when writing c_k^* in (27). Substituting the matrix (26) into (1), (4) and (7) with (27) and the condition of incompressibility of the medium taken into account, we obtain

$$\begin{gathered} \dot{c}_{k,11} + (4\theta_k)^{-1} \exp(m_k W_k)(c_k - c_k^{-1})[c_k - c_k^{-1} + \\ + (c_k + c_k^{-1})\cos 2\varphi_k] = 2\dot{\gamma} c_{k,12}, \\ \dot{c}_{k,12} + (4\theta_k)^{-1} \exp(m_k W_k)(c_k - c_k^{-1})(c_k + c_k^{-1})\sin 2\varphi_k = \dot{\gamma} c_{k,22}, \\ 2c_{k,11} = c_k + c_k^{-1} + (c_k - c_k^{-1})\cos 2\varphi_k, \\ 2c_{k,22} = c_k + c_k^{-1} - (c_k - c_k^{-1})\cos 2\varphi_k,\ \ 2c_{k,12} = (c_k - c_k^{-1})\sin 2\varphi_k. \end{gathered} \tag{28}$$

Taking into account that $c_k^{n_k/2} = q_k \cdot c_k^{*\,n_k/2} \cdot q_k^{-1}$, an expression can be obtained for the components of the stress tensor (3) and (8) in terms of c_k and φ_k.

The following quantities are ordinarily measured in experiments with polymer liquids

$$\begin{gathered} \sigma_1 = \sigma_{11} - \sigma_{22} = 4 \sum_k \left(\frac{\mu_k}{n_k}\right)(c_k^{n_k/2} - c_k^{-n_k/2})\cos 2\varphi_k, \\ \sigma_2 = \sigma_{22} - \sigma_{33} = 2 \sum_k \left(\frac{\mu_k}{n_k}\right)[c_k^{n_k/2} + c_k^{-n_k/2} - 2 - (c_k^{n_k/2} - c_k^{-n_k/2})\cos 2\varphi_k], \\ \sigma_{12} = 2 \sum_k \left(\frac{\mu_k}{n_k}\right)(c_k^{n_k/2} - c_k^{-n_k/2})\sin 2\varphi_k. \end{gathered} \tag{29}$$

In the case of the stationary flow (28) (for $\dot{\gamma} = \text{const}$)

$$\begin{gathered} \cos 2\varphi_k = \frac{c_k - c_k^{-1}}{c_k + c_k^{-1}},\ \ \sin 2\varphi_k = \frac{2}{c_k + c_k^{-1}}, \\ (c_k + c_k^{-1})(c_k - c_k^{-1})\exp(m_k W_k) = 4\theta_k \dot{\gamma} \end{gathered} \tag{30}$$

and (29) takes the form

$$\begin{gathered} \sigma_{12} = \sum_k \sigma_{12}^{(k)} = 4 \sum_k \left(\frac{\mu_k}{n_k}\right)(c_k^{n_k/2} - c_k^{-n_k/2})(c_k + c_k^{-1})^{-1}, \\ \sigma_1 = \sum_k \sigma_1^{(k)} = \sum_k \sigma_{12}^{(k)}(c_k - c_k^{-1}), \\ \sigma_2 = 2 \sum_k \left(\frac{\mu_k}{n_k}\right)\left[c_k^{n_k/2} + c_k^{-n_k/2} - 2 - \frac{\sigma_1^{(k)} n_k}{4\mu_k}\right]. \end{gathered}$$

The elastic potential (see (6)) for each Maxwell element under simple shear is

$$W_k = \frac{4\mu_k}{n_k^2}(c_k^{n_k/2} + c_k^{-n_k/2} - 2).$$

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†We follow [2] in the further examination of Sec. 4.

Let us consider the asymptotic dependences of σ_{12}, σ_1 and σ_2 on the dimensionless parameters $\Gamma_k = \dot{\gamma}\theta_k$ for $m_k W_k \ll 1$ by following [2]

$$\max \Gamma_k \ll 1,\ \sigma_{12} \approx \eta\dot{\gamma},\ \eta = \sum_k \eta_k,$$

$$\sigma_1 \approx 4 \sum_k \mu_k \theta_k^2 \dot{\gamma}^2,\ \sigma_2 \approx -2 \sum_k \mu_k \theta_k^2 \left(1 - \frac{n_k}{4}\right) \dot{\gamma}^2, \tag{31}$$

$$\min \Gamma_k \gg 1,\ \sigma_{12} \approx 4 \sum_k \left(\frac{\mu_k}{n_k}\right) (4\Gamma_k)^{\frac{n_k-2}{4}},$$

$$\sigma_1 \approx 4 \sum_k \left(\frac{\mu_k}{n_k}\right) (4\Gamma_k)^{\frac{n_k}{4}}, \tag{32}$$

$$\sigma_2 \approx -4 \sum_k \left(\frac{\mu_k}{n_k}\right) [1 - (4\Gamma_k)^{-\frac{n_k}{4}} - (4\Gamma_k)^{\frac{n_k-4}{4}}].$$

In order to obtain a correspondence with experiment $(\sigma_2^{(k)} < 0,\ d(\sigma_{12}^{(k)}/\Gamma_k)/d\Gamma_k < 0)$, for each Maxwell element, we assume* $4 \geq n_k \geq 2$, as in [2]. For $n_k < 2$ the dependence $\sigma_{12}^{(k)}(\Gamma_k)$ passes through a maximum. The descending branch is unstable in this case.

In the case of small amplitude shear vibrations in the linear strain domain, the following are the expressions for the elastic and loss moduli for Maxwell models connected in parallel

$$G' = 2 \sum_k \mu_k \frac{(\omega\theta_k)^2}{1 + (\omega\theta_k)^2},$$

$$G'' = 2 \sum_k \mu_k \frac{\omega\theta_k}{1 + (\omega\theta_k)^2}. \tag{33}$$

Uniaxial homogeneous tension is usually realized for the tension of a cylinder of a polymer liquid. This kind of strain is given in a fixed Cartesian coordinate system by the matrices ($\varkappa > 0$ is the strain rate)

$$\mathbf{e} = \varkappa \operatorname{diag}\left\{1,\ -\frac{1}{2},\ -\frac{1}{2}\right\},\ \omega \equiv 0,\ \mathbf{c}_k = \operatorname{diag}\{\lambda_k^2,\ \lambda_k^{-1},\ \lambda_k^{-1}\}. \tag{34}$$

The condition of incompressibility of the medium (2) is taken into account in the expressions for the tensors **e** and $\mathbf{c}_k$. Substituting the matrices (34) into (1)-(8) we obtain a system of governing equations for the tension

$$\frac{\theta_k}{\lambda_k} \frac{d\lambda_k}{dt} + \exp(m_k W_k) \frac{(\lambda_k + 1)(\lambda_k^3 - 1)}{6\lambda_k^2} = \varkappa\theta_k,$$

$$\sigma = 4 \sum_k \frac{\mu_k}{n_k} (\lambda_k^{n_k} - \lambda_k^{-n_k/2}),\ W_k = \frac{4\mu_k}{n_k^2} (\lambda_k^{n_k} + 2\lambda_k^{-n_k/2} - 3), \tag{35}$$

where σ is the tensile stress. It was assumed in the derivation of the second formula in (35) that the stress vanishes on the free surface of the cylinder under tension.

The asymptotic behavior of the stress σ as a function of the dimensionless parameters $\Gamma_k = \dot{\gamma}\theta_k$ ($m_k W_k \ll 1$) is

$$\max \Gamma_k \ll 1 : \sigma \approx 3\eta\varkappa,$$

$$\min \Gamma_k \gg 1 : \sigma \approx 4 \sum_k \left(\frac{\mu_k}{n_k}\right) (6\Gamma_k)^{\frac{n_k}{2}}. \tag{36}$$

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*This condition is conserved even for $m_k \neq 0$.

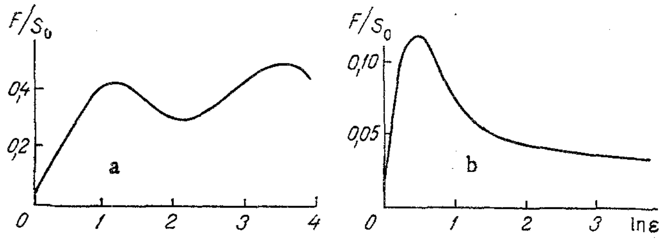

Fig. 1. Dependences of the tensile forces referred to the area of the specimen initial section F/S_0 (Pa) on the total strain $\ln \varepsilon$: a) $\kappa = 1.2 \cdot 10^{-2}$, b) $\kappa = 1.2 \cdot 10^{-3}$ ($\sec^{-1}$).

5. LARGE RELAXATION TIME WITH SMALL WEIGHT

The case is considered when the inequality

$$\eta_1 \ll \sum_{k=2}^{N} \eta_k,$$

is also satisfied as well as (15)-(17), i.e., a large relaxation time θ_1 with small weight[†] corresponds to the first relaxation mechanism. If only two mechanisms are taken into account, then $\sum_{k=2}^{N} \eta_k = \eta_2$; if subsequent mechanisms are also taken into account, then, as usual [2], the inequalities $\eta_k > \eta_{k+1}$ are satisfied for them for $k > 2$.

It is simplest to investigate the influence of a coarse-scale mechanism with small weight on the motion in stationary cases. Moreover, if the coarse-scale relaxation mechanism is not essential in stationary motion under shear and tension, then it is also not essential in the prestationary domain. For simplicity we shall also consider that $m_k W_k \ll 1$, $n_k \equiv n$, and $N = 2$.

We start with simple shear. Since $\eta_1 \ll \eta_2$ and the effective viscosity under strain with a constant shear rate $\dot{\gamma}$ $\eta_k^* = \sigma_{k,12}/\dot{\gamma}$ (see (31) and (32) as $\dot{\gamma} \to 0$ $\eta_k^* \to \eta_k$; for $\Gamma_k \gg 1$ $\eta_k^* \approx 8\eta_k/n_k (4\Gamma_k)^{\frac{6-n_k}{4}}$) decreases in each Maxwell element as γ grows, then the coarse-scale mechanism does not affect the dependences $\sigma_{12}(\dot{\gamma})$ (and the nonstationary dependences $\sigma_{12}(t)/\dot{\gamma}$). It is also not reflected in the dependence $G''(\omega)$ (see (33)) which agrees as $\omega \to 0$ with $\sigma_{12}(\dot{\gamma})$ for $\gamma = \omega$.

By virtue of the inequality $\eta_1\theta_1 \gg \eta_2\theta_2$ (see (17) and (31)), the coarse-scale mechanism will yield a substantial contribution to the normal stress for $\Gamma_1 \ll 1$. As the strain rate increases the coefficient $\alpha_* = \sigma_1/\dot{\gamma}^2$ (see (32)) diminishes ($\dot{\gamma} \to 0$, $\alpha_* \approx 4\mu_k\theta_k^2 = 2\eta_k\theta_k$; for $\Gamma_k \gg 1$ $\alpha_{*,k} = 32\eta_k\theta_k / n_k (4\Gamma_k)^{\frac{8-n_k}{4}}$) and the role of the coarse-scale mechanism drops. This mechanism can be clarified also by dynamic tests for $\omega\theta_1 \ll 1$, where $G'(\omega) = \sigma_1(\dot{\gamma} = \omega)/2$ (see (33)).

Simple shear tests to clarify the coarse-scale relaxation mechanism for small dimensionless frequencies and strain rates (for instance if $\theta_1 \sim 10^4$ sec) are sufficiently complex although there is information (see [15]) that such times have been measured successfully in dynamic tests.

The time to achieve stationary motion (γ = const) for $\sigma_1(t)$ can be protracted considerably (because of the coarse-scale mechanism) as compared with $\sigma_{12}(t)$. Experiments to measure the development of normal stresses in time for highly viscous media are complex for any γ because of the ordinarily large characteristic time of the measurement facilities [7].

However, under uniaxial tension the coarse-scale mechanism appears considerably more clearly than under shear in a substantially nonlinear domain of medium behavior. This occurs because the effective viscosity in a stationary flow $(\varkappa = \mathrm{const})$ $\xi_k^* = \sigma_k/\varkappa$ (see (36))

[†] Theoretically a coarse-scale mechanism with small weight is predicted in [13, 14] for monodisperse polymers. The nature of such mechanisms can apparently be distinct.

increases as the dimensionless strain rate grows $\Gamma_k = \varkappa\theta_k$ ($\varkappa \to 0$, $\xi_k^* \to 3\eta_k$; $\Gamma_k \gg 1$, $\xi_k^* \approx 12\eta_k (6\Gamma_k)^{(n_k-2)/2}/n_k$). Consequently, the viscosity ξ_1^* can become significantly greater than $3\eta_2$ in the domain wnere $\Gamma_1 \gg 1$ and $\Gamma_2 \ll 1$. Let us recall that for $\Gamma_1 \ll 1$ $\xi_1^* \simeq \eta_1 \ll \eta_2$.

Let us examine the most clear appearance of the coarse-scale mechanism in the prestationary strain domain under tension in the regime κ = const. In this case (35) with the initial conditions $t = 0$, $\lambda_1 = 1$, $\lambda_2 = 1$ were solved numerically for $n_1 = n_2 = 3.6$; $\theta_1 = 8 \cdot 10^3$ sec, $\theta_2 = 10^2$ sec, $\mu_1 = 4.4$ Pa, $\mu_2 = 1.5 \cdot 10^3$ Pa, $m_1 = m_2 = 0$. Shown in the figure are the dependences of the tensile force F referred to the area of the initial section S_0 on the logarithmic measure of the total strain $\ln \varepsilon = \kappa t$. As usual, for small strain rates one maximum is in these dependences and for large, two. This effect was first observed experimentally in [9]. The second maximum is a consequence of exposure during motion of the coarse-scale mechanism. Because of this mechanism the time to achieve stationary flow can be protracted substantially as compared with the shear dependences.

In conclusion, let us note that the mechanism of potential barrier distortion by stress during tension can turn out also to be substantial because the stress here grows more intensively than under shear. This mechanism results in the passage of the effective viscosity dependence under stationary tension on the strain rate through the maximum, as was observed experimentally in [16].

NOTATION

$\mathbf{c}_k$ and H_k, elastic strain tensors (Finger and Henke measures) in the k-th Maxwell element; $\mathbf{e}$ and $\boldsymbol{\omega}$, strain rate and vortex tensors; $\mathbf{e}_{p,k}$, irreversible strain rate tensor; $\boldsymbol{\sigma}_k$, stress tensor; n_k, a constant characterizing the degree of the elastic potential; μ_k, elastic modulus; θ_k^*, θ_k and $\theta_{0,k}$, relaxation times; $I_{1,k}$ and $I_{2,k}$, invariants of the tensor $\mathbf{c}_k$; $\mathbf{E}$, unit tensor; f_k, f, u_k, u, specific, free, and internal energies; s, s_k, specific entropies; ρ, density; W_k, elastic potential; T, temperature; E_k, viscous flow activation energy; γ_k and m_k, constants; R, universal gas constant; N, number of Maxwell elements connected in parallel; P, pressure; $\boldsymbol{\sigma}$, total stress tensor in the system; η_{k*}, viscosity; s_*, ratio of the retardation time to the relaxation time; η, greatest Newtonian viscosity; c, specific heat; t, time; Q, quantity of heat; $\tilde{\kappa}$, heat-conduction coefficient; $\bar{s}_k$, $\tilde{s}_k$, specific entropy components; $\dot{\gamma}$, shear rate, $c_{k,ij}$, components of the tensor $\mathbf{c}_k$; σ_1, σ_2 and σ_{12}, first and second differences of the normal stresses and the tangential stress under simple shear; $\mathbf{q}_k$ and φ_k, orthogonal transformation and the corresponding angle of rotation; c_k, component of the tensor $\mathbf{c}_k$ reduced to diagonal form; Γ_k, dimensionless strain rate; G' and G'', elastic and loss moduli determined under low-amplitude vibrations; κ, tension strain rate; λ_k, relative elongation; η_k^* and ξ_k^*, effective viscosity under shear and tension; ω, frequency of vibration.

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