POLYMER MECHANICS

МЕХАНИКА ПОЛИМЕРОВ

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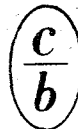
EQUATIONS OF MOTION OF VISCOELASTIC SYSTEMS
AS DERIVED FROM THE CONSERVATION LAWS AND
THE PHENOMENOLOGICAL THEORY OF
NONEQUILIBRIUM PROCESSES

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The system of equations of motion for a liquid and a solid with internal parameters — scalars and second-order tensors — is written out in the linear approximation. From the system of equations for the class of motions with velocity gradients independent of the coordinates there follows the known equation of the linear theory of viscoelasticity. It is shown that the correct description of the motions of polymer systems requires a quadratic approximation. A nonlinear variant of the theory of viscoelasticity, in which spectral functions that depend on the internal parameters are introduced, is proposed.

The dynamic properties of polymeric systems are associated with the relaxation processes that accompany deformation of the system and, accordingly, a natural physical basis for the development of phenomenological theories of the motion of viscoelastic systems is provided by the theory of nonequilibrium processes, which makes use of an important assumption, going back to Mandel'shtam and Leontovich [1], concerning the existence of certain internal parameters describing the deviation of the system from equilibrium and, together with the thermodynamic parameters, characterizing its state. Many authors [2] have discussed the theory of viscoelasticity from this standpoint, but, since it is necessary to make an a priori assumption concerning the number and tensor dimensionality of the internal parameters, the phenomenological equations of motion of viscoelastic systems cannot be formulated in such general form as, for example, the equations of motion of a viscous fluid. In particular, as a rule, the investigation is confined to the case when all the internal parameters are scalars [2], which does not apply to the systems of of interest to us. Below, on the basis of the theory of nonequilibrium processes [2] a phenomenological theory of viscoelasticity is progressively developed in a form suitable for describing the motion of polymeric systems.

1. In order to clarify the physical significance of the relaxation processes accompanying deformation and determine the nature of the internal variables, it is necessary to consider the results of the structural theories of motion of polymeric systems.

A dilute polymer solution can be simulated by a suspension of ideally flexible strings of identical, equally spaced beads moving in a liquid with viscosity η. An elasticity force acts between adjacent beads, and in motion each bead experiences hydrodynamic resistance, so that it is possible to introduce the bead friction coefficient ζ. It has been shown [3] that the stress tensor of the suspension has the form

$$\sigma_{ik} = -p\delta_{ik} + 2\eta(1+1.5\varphi)v_{(ik)} + \frac{1}{2}n\zeta\sum_{\alpha}\frac{1}{\tau_\alpha}(\langle\rho_i{}^\alpha\rho_k{}^\alpha\rangle - \langle\rho_i{}^\alpha\rho_k{}^\alpha\rangle_0), \tag{1.1}$$

where p is pressure; φ is the characteristic volume concentration of the beads; $v_{ik} = \partial v_i/\partial x_k$ is the velocity gradient tensor; n is the number density of the macromolecules; τ_α are relaxation times; $\rho_i{}^\alpha$ is the

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normal coordinate associated with the motion of the beads; and $\langle \rho_i{}^\alpha \rho_k{}^\alpha \rangle$ are the moments of the distribution function, which satisfy the equation

$$\frac{d\langle \rho_i{}^\alpha \rho_k{}^\alpha \rangle}{dt} = -\frac{1}{\tau_\alpha}(\langle \rho_i{}^\alpha \rho_k{}^\alpha \rangle - \langle \rho_i{}^\alpha \rho_k{}^\alpha \rangle_0) + v_{ij}\langle \rho_k{}^\alpha \rho_j{}^\alpha \rangle + v_{kj}\langle \rho_j{}^\alpha \rho_i{}^\alpha \rangle. \tag{1.2}$$

Taken together, the $\langle \rho_i{}^\alpha \rho_k{}^\alpha \rangle$ describe the shape and size of the deformed coil and in the case in question constitute the internal parameters.

Results similar in form were obtained in [4] for regular networks with stable nodes connecting four chains. An analysis of the motion of the network nodes as centers of friction yielded the following expression for the stress tensor

$$\sigma_{ih} = \sigma_{ih}{}^0 + 2\eta v_{(ih)} + \frac{1}{2}v\zeta \frac{1}{2N^3}\sum_\alpha \frac{1}{\tau_\alpha}(\langle \rho_i{}^\alpha \rho_k{}^\alpha \rangle - \langle \rho_i{}^\alpha \rho_k{}^\alpha \rangle_0), \tag{1.3}$$

where $\sigma_{ik}{}^0$ is the elastic stress tensor; η is the effective coefficient of viscosity of the monomer units; ν is the number density of the nodes; $2N^3$ is the number of nodes in the specimen. As before, the equation for the moments of the distribution function takes the form (1.2); however, in this case, of course, the set of relaxation times is essentially different. Thus, here too, the internal variables are the second-order tensors $\langle \rho_i{}^\alpha \rho_k{}^\alpha \rangle$, which together describe the deviation of the nodes from the positions that they would have occupied under equilibrium deformation conditions.

In addition to these tensor parameters, the system may also be defined by scalar parameters. In fact, in considering concentrated polymer solutions and melts, it is necessary to take into account the relaxation processes associated with the destruction and formation of labile nodes [5]. These processes are analogous to chemical reactions, which, as is known [2], are described by scalar internal variables.

2. The thermodynamic state of a single-component system in equilibrium is described by three parameters, for example, density ρ (or specific volume ν), pressure p, and temperature T. Since, in principle, there is always an equation of state relating these quantities $f(T, p, \rho) = 0$, two of the three parameters are sufficient for the complete characterization of a system in equilibrium.

The equilibrium change of internal energy E of unit volume of a homogeneous system is related with the changes of entropy s per unit mass by the known [6] formula

$$dE = \rho T ds + w\, d\rho, \tag{2.1}$$

where w is the enthalpy of unit mass.

If the system is in uniform rectilinear motion, obviously, thermodynamic equilibrium is not disturbed. However, if there are velocity gradients and displacement gradients, then, generally speaking, the deformed system is no longer in equilibrium, even locally.

In the presence of slow external changes the internal processes may be able to follow the change in the state of the system. In other words, all the relaxation times are small as compared with the times characterizing the motion of the system. This applies to low-viscosity fluids, in which equilibrium can be established in the process of motion, and equilibrium equation (2.1) is used for the change of energy of a volume element. In the process of motion the state of the system is determined, apart from velocity, by density and temperature only. In flow the system remains isotropic. As is known [6], the consistent development of a phenomenological theory of motion of such systems leads to the system of Navier–Stokes equations describing the motion of low-viscosity fluids.

When the motion is more rapid, certain internal processes are unable to follow the external changes. The process of deformation proceeds in a nonequilibrium manner, and in this case the state of the system is additionally described by certain internal independent variables ξ. This is now the generally accepted view [2, 7].

The thermodynamic functions of the system now depend on the internal variables. For example, the internal energy of unit volume $E = E(s, p, \xi^\alpha)$

$$dE = \rho T ds + w\, d\rho + TX_\alpha d\xi^\alpha, \tag{2.2}$$

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where $X_\alpha = \frac{1}{T}\left(\frac{\partial E}{\partial \xi^\alpha}\right)_{s,\rho} = -\left(\frac{\partial(\rho s)}{\partial \xi^\alpha}\right)_{E,\rho} > 0$. The quantities T, w, and X_α are functions of the variables s, ρ, and ξ^α. In the equilibrium state all $\xi^\alpha = \xi_e{}^\alpha$, and in this case T and w take their equilibrium values, while $X_\alpha = 0$, so that at small ξ^α the thermodynamic forces X_α can be expanded in a series that begins with a first-order term. In the first approximation

$$X_\alpha = \beta_{\alpha\gamma}(\xi^\gamma - \xi_e{}^\gamma). \tag{2.3}$$

Henceforth we shall simply write ξ^α, by which we understand $\xi^\alpha - \xi_e{}^\alpha$. In this case it should be kept in mind that the $\xi_e{}^\alpha$ may change during motion.

The internal parameters may have different tensor orders. We will consider the case when the internal parameters are scalars and second-order symmetrical tensors. If the system has only two of these parameters, then as the variables it is convenient to employ the quantities ξ, ξ_{jj}, $\xi_{ik}' = \xi_{ik} - \frac{1}{3}\xi_{jj}\delta_{ik}$, which correspond to the "thermodynamic forces" X, X_{jj}, $X_{ik}' = X_{ik} - \frac{1}{3}X_{jj}\delta_{ik}$. The relations between them take the form

$$X = \beta_1\xi + \beta_2\xi_{jj}; \quad X_{jj} = 3\beta_3\xi + 3\beta_4\xi_{jj}; \quad X'_{ik} = \beta_5\xi'_{ik}. \tag{2.4}$$

3. The equations of motion of a continuum are found as a consequence of the laws of conservation of mass, momentum, energy, and angular momentum. In this case, assuming the medium to be single-component, we shall not consider diffusion processes.

We write the law of conservation of mass in the continuity equation form

$$\frac{\partial \rho}{\partial t} + \operatorname{div}\rho\mathbf{v} = 0. \tag{3.1}$$

Here, $\rho\mathbf{v}$ is the mass flux density. In the absence of extraneous body forces the law of conservation of momentum takes the form

$$\frac{\partial \rho v_i}{\partial t} + \frac{\partial \Pi_{ik}}{\partial x_k} = 0 \tag{3.2}$$

(Π_{ik} is the momentum flux density tensor); the law of conservation of energy is written

$$\frac{\partial E}{\partial t} + \operatorname{div}\mathbf{Q} = 0 \tag{3.3}$$

(Q is the energy flux density), and in the absence of extraneous distributed moments of force the law of conservation of total angular momentum takes the form

$$\frac{\partial}{\partial t}(L_{ik} + S_{ik}) + \frac{\partial G_{ikl}}{\partial x_l} = 0, \tag{3.4}$$

where $L_{ik} = \rho(x_i v_k - x_k v_i)$ is the external angular momentum flux density; S_{ik} is the internal angular momentum flux density; G_{ikl} is the total angular momentum flux density. Moreover, we must add the law of variation of S_{ik}

$$\frac{\partial S_{ik}}{\partial t} + \frac{\partial}{\partial x_l}(v_l S_{ik}) = K_{ik}, \tag{3.5}$$

where K_{ik} is the moment density of the forces acting on the fluid particles, and the equation for the variation of the entropy density ρs

$$\rho\left(\frac{\partial s}{\partial t} + v_i\frac{\partial s}{\partial x_i}\right) + \operatorname{div}H = \sigma, \tag{3.6}$$

where H_i is the nonconvective entropy flux density; σ is the entropy production.

We express the momentum flux density in terms of the stress tensor $\Pi_{ik} = \rho v_i v_k - \sigma_{ik}$, after which we rewrite Eq. (3.2) in the form

$$\rho\left(\frac{\partial v_i}{\partial t} + v_k\frac{\partial v_i}{\partial x_k}\right) = \frac{\partial \sigma_{ik}}{\partial x_k}. \tag{3.7}$$

We write the external angular momentum flux density as follows: $L_{ik}v_j = x_i(\Pi_{kj} + \sigma_{kj}) - x_k(\Pi_{ij} + \sigma_{ij})$ and express the change of external angular momentum in terms of σ_{ik}

$$\frac{\partial L_{ik}}{\partial t} + \frac{\partial}{\partial x_l}(v_l L_{ik}) = \sigma_{ik} - \sigma_{ki} + \frac{\partial}{\partial x_l}(x_i \sigma_{kl} - x_k \sigma_{il}).$$ (3.8)

Summing Eqs. (3.5) and (3.8) and comparing the equation obtained with (3.4), we find

$$G_{ikl} = (L_{ik} + S_{ik})v_l - (x_i \sigma_{kl} + x_k \sigma_{il});$$ (3.9)

$$K_{ik} = -2\sigma_{[ik]}.$$ (3.10)

From the latter equation it follows that the nonsymmetry of the stress tensor is associated with the presence of moments of the forces acting on the fluid particles. If there are no internal moments, the law of conservation of angular momentum is automatically satisfied, being a consequence of the law of conservation of momentum.

Thus, the three unknown tensors in Eq. (3.2), (3.4), and (3.5) are expressed in terms of the stress tensor. All the expressions obtained so far are general in character and are not related to any specific material. However, in what follows, in order to determine the unknown entropy production functions and energy flux densities, it will be necessary to employ the expression for the change of energy density of a particular system.

4. We will start by considering the motion of a viscous fluid on the assumption that there are no internal relaxation processes, i.e., locally the fluid is in equilibrium. The kinetic energy of unit volume of the moving fluid (without allowance for the kinetic energy of the internal degrees of freedom) is equal to $\rho v^2/2$ and, accordingly, using expression (2.2), we write the change of total energy per unit volume of the moving fluid in the form

$$\frac{\partial E}{\partial t} = \rho v_i \frac{\partial v_i}{\partial t} + \rho T \frac{\partial s}{\partial t} + \left(w + \frac{v^2}{2}\right)\frac{\partial \rho}{\partial t}.$$ (4.1)

On the right side of the latter equation we substitute the time derivatives given by expressions (3.1) and (3.7) and after certain transformation obtain

$$\frac{\partial E}{\partial t} + \frac{\partial}{\partial x_k}\left[\rho v_k\left(w + \frac{v^2}{2}\right) - v_i \sigma_{ik}\right] = \rho v_i \frac{\partial w}{\partial x_i} - \sigma_{ik}\frac{\partial v_i}{\partial x_k} + \rho T \frac{\partial s}{\partial t}.$$

Using the thermodynamic relation

$$dw = T ds + \frac{1}{\rho} dp$$ (4.2)

we write the right side of the last equation in the form

$$\rho T\left(\frac{\partial s}{\partial t} + v_i \frac{\partial s}{\partial x_i}\right) - \sigma_{ik}\frac{\partial v_i}{\partial x_k} + v_i \frac{\partial \rho}{\partial x_i}.$$

We then transform the last term and, using (3.6), obtain an equation which we compare with (3.3). Hence we obtain

$$Q_k = \rho v_k\left(w + \frac{v^2}{2}\right) - v_i(\sigma_{ik} + p\delta_{ik}) + TH_k;$$ (4.3)

$$\sigma = (\sigma_{ik} + p\delta_{ik})\frac{1}{T}v_{ik} - H_i \frac{1}{T}\nabla_i T.$$ (4.4)

Thus, all the unknown functions have been determined in terms of the stress tensor and the entropy flux density.

In the case considered the presence of a velocity gradient v_{ik} and a temperature gradient $\nabla_i T$, which determine the fluxes $\sigma_{ik} + p\delta_{ik}$ and H_i, leads to irreversible processes. As functions of the gradients the fluxes are not given in general form, but at small gradients they can be determined as expansions in the small gradients. If we further require that rotation at constant velocity of the liquid as a whole does not affect the stress tensor, then correct to terms of the first order we find

$$\sigma_{ik} + p\delta_{ik} = 2\eta v'_{(ik)} + \zeta \delta_{ik} v_{jj};$$ (4.5)

$$H_i = -\frac{\varkappa}{T}\nabla_i T,$$ (4.6)

where we have introduced the notation $v'_{(ik)} = v_{(ik)} - \frac{1}{3}\delta_{ik}v_{jj}$. In order to ensure the positiveness of σ, the constants η, ζ, $\varkappa$ must be positive.

The substitution of expressions (4.5) in (3.7) leads to the equation of motion of a viscous fluid — the Navier—Stokes equation, which, when the coefficients of viscosity do not depend on the space coordinates, takes the form

$$\rho\frac{dv_i}{dt} = -\frac{\partial p}{\partial x_i} + \eta\frac{\partial^2 v_i}{\partial x_k^2} + \left(\frac{1}{3}\eta + \zeta\right)\frac{\partial^2 v_k}{\partial x_i \partial x_k}. \tag{4.7}$$

After substituting expressions (4.5) and (4.3), with allowance for the former, in (3.6), we obtain the energy transfer equation

$$\rho T\left(\frac{\partial s}{\partial t} + v_i\frac{\partial s}{\partial x_i}\right) = \operatorname{div}(\varkappa\nabla T) + (\sigma_{ik} + p\delta_{ik})v_{ik}. \tag{4.8}$$

Together with continuity Eq. (3.1), expressions (4.7) and (4.8) form a complete system of equations for describing the motion of a viscous fluid.

5. We will now consider the motion of a system characterized by certain internal parameters. Using (2.2), we write the change internal energy in the form

$$\frac{\partial E}{\partial t} = \rho v_i\frac{\partial v_i}{\partial t} + \rho T\frac{\partial s}{\partial t} + \left(w + \frac{v^2}{2}\right)\frac{\partial\rho}{\partial t} + TX_\alpha\frac{\partial\xi^\alpha}{\partial t}. \tag{5.1}$$

Proceeding as before, with the aid of Eqs. (3.1), (3.6), and (3.7) we transform Eq. (5.1) to an equation that has the form of the law of conservation of energy; in this case, instead of (4.2), we use the relation $dw = Tds + \frac{1}{\rho}dp + \frac{T}{\rho}X_\alpha d\xi^\alpha$. Eventually, we obtain

$$\frac{\partial E}{\partial t} + \frac{\partial}{\partial x_k}\left[\rho v_k\left(w + \frac{v^2}{2}\right) - v_i(\sigma_{ik} + p\delta_{ik}) + TH\right] = T\sigma - (\sigma_{ik} + p\delta_{ik})v_{ik} + H_i\nabla_i T + T\frac{d\xi^\alpha}{dt}X_\alpha. \tag{5.2}$$

Comparing this equation with (3.3), we find that, as before, the energy flux takes the form (4.3), while the entropy production

$$\sigma = (\sigma_{ik} + p\delta_{ik})\frac{1}{T}v_{ik} - H_i\frac{1}{T} - \frac{d\xi^\alpha}{dt}X_\alpha. \tag{5.3}$$

We will consider the simple case when the motion of the system is determined by two internal parameters — the scalar ξ and the second-order symmetrical tensor ξ_{ik}. Then the last term in Eq. (5.3) is rewritten in the form $-(d\xi/dt)X - (d\xi_{ik}/dt)X_{ik}$. The fluxes $\sigma_{ik} + p\delta_{ik}$, $-H_i$, $-d\xi/dt$, $-d\xi_{ik}/dt$ are functions of the "thermodynamic forces" $(1/T)v_{ik}$, $(1/T)\nabla_i T$, X, X_{ik} and in the linear approximation, if it is further assumed that rotation of the system as a whole does not produce any changes in the system, take the form

$$-H_i = \varkappa\frac{1}{T}\nabla_i T; \tag{5.4}$$

$$\sigma_{ik} + p\delta_{ik} = 2\eta v'_{(ik)} + \zeta v_{jj}\delta_{ik} - \alpha_{02}TX_{ik} - \mu_{01}TX\delta_{ik} - \mu_{02}TX_{jj}\delta_{ik};$$

$$-\frac{d\xi}{dt} = -\mu_{10}v_{jj} + \mu_{11}X + \mu_{12}X_{jj};$$

$$-\frac{d\xi_{ik}}{dt} = -\alpha_{20}v'_{(ik)} + \alpha_{22}X'_{ik} - \mu_{20}v_{jj}\delta_{ik} + \mu_{21}X\delta_{ik} + \mu_{22}X_{jj}\delta_{ik}. \tag{5.5}$$

By virtue of the principle of symmetry of the kinetic coefficients [2, 7] $\alpha_{02} = \alpha_{20}$; $\mu_{\alpha\beta} = \mu_{\beta\alpha}$. Thus, of the 14 coefficients in Eqs. (5.4) and (5.5) 10 are independent, the condition of nonnegativity of the entropy production imposing certain limitations on their values.

We now write the fluxes in terms of the internal parameters. In this case expression (5.4) remains unchanged, while, using (2.4), we can rewrite (5.5) in the form

$$\sigma_{ik} + p\delta_{ik} = 2\eta v'_{(ik)} + \zeta v_{jj}\delta_{ik} + \frac{\gamma}{\tau}\xi'_{ik} + \omega_1\xi\delta_{ik} + \omega_2\xi_{jj}\delta_{ik}; \tag{5.6}$$

$$\frac{d\xi'_{ik}}{dt} = \alpha_{20}v'_{(ik)} - \frac{1}{\tau}\xi'_{ik}; \tag{5.7}$$

$$\frac{d\xi}{dt} = \mu_{10}v_{jj} - \lambda_{11}\xi - \lambda_{12}\xi_{jj}; \qquad \frac{d\xi_{jj}}{dt} = 3\mu_{20}v_{jj} - \lambda_{21}\xi - \lambda_{22}\xi_{jj}, \tag{5.8}$$

where $\gamma/\tau = \alpha_{02}\beta_4$, and the coefficients ω_1, ω_2, and $\lambda_{\alpha\beta}$ are related in a certain way with the constants previously introduced. If the matrix $\lambda_{\alpha\beta}$ can be reduced to diagonal form, then instead of (5.8) we obtain

$$\frac{d\xi}{dt} = \mu_{10}v_{jj} - \frac{1}{\tau}\xi; \qquad \frac{d\xi_{jj}}{dt} = 3\mu_{20}v_{jj} - \frac{1}{\tau_2}\xi_{jj}. \tag{5.9}$$

If the velocity gradients disappear, then each of Eqs. (5.7) and (5.9) assumes the form: $d\xi^\alpha/dt = -(1/\tau_\alpha)\xi^\alpha$. This equation describes the approach of the system to equilibrium. The constants τ_α determine the rate of approach of the system to equilibrium and have the significance of relaxation times.

If all the relaxation times of the system are equal to zero, then the values of the internal parameters are always equal to the equilibrium values, and the system of equations of motion reduces to the system formulated in the previous section. In the general case, substituting (5.6) in (3.7), we obtain the equation of motion of a medium with scalar and tensor internal parameters

$$\rho\frac{dv_i}{dt} = \frac{\partial p}{\partial x_i} + \eta\frac{\partial^2 v}{\partial x_h^2} + \left(\frac{1}{3}\eta + \zeta\right)\frac{\partial^2 v_k}{\partial x_i \partial x_h} + \frac{\gamma}{\tau}\frac{\partial \xi'_{ik}}{\partial x_h} + \omega_1\frac{\partial \xi}{\partial x_i} + \omega_2\frac{\partial \xi_{jj}}{\partial x_i}. \tag{5.10}$$

Together with continuity Eq. (3.1), heat transfer Eq. (4.9), and the laws of variation of the internal parameters (5.7) and (5.9), Eq. (5.10) completely determines the behavior of the system in the linear approximation. The coefficients in Eqs. (5.4), (5.6), and (5.9) are material constants of the system.

This system of equations can be written in another form if the internal parameters are eliminated, which is possible in principle. In this case the system reduces to a system of fewer, but higher-order equations.

The number and physical significance of the material constants introduced by relations of type (5.6), (5.7), and (5.9), the form of the equations of motion and, consequently, the properties of the system depend importantly on the tensor order of the internal variables, which can thus be used to classify viscoelastic systems.

6. Sometimes certain relaxation processes in the system are so slow that a noticeable change does not take place during the observation period, i.e., the relaxation times of these processes may be considered infinitely large. In this case the values of the internal parameters and hence the stress tensor are uniquely determined by the shape and volume of the specimen. Thermodynamic concepts can be used to describe the partial equilibrium state of a deformed system.

Let x_i^0 be the Cartesian coordinate of some point of a body before deformation; of course, the coordinate x_k of the same point after deformation is a function of the initial point $x_k = x_k(x_j^0)$. The deformation vector is defined as the difference $u_i = x_i - x_i^0$.

Considering an arbitrary deformation, we write the change of the small distance $dx_i = (dx_i/dx_k^0)dx_k^0 = \lambda_{ik}dx_k^0$, length $(dl)^2 = \lambda_{ik}\lambda_{il}dx_k^0 dx_l^0$, and volume $dv = |\lambda|dv_0$. Following Flory [8], we select the symmetrical tensor $\Lambda_{kj} = \lambda_{ij}\lambda_{ik}$ as our measure of large deformations.

Let σ_{ik} — the tensor of the stresses referred to the deformed body — be the true stress tensor. The force acting on unit volume is written in the form

$$F_i = \frac{\partial \sigma_{ik}}{\partial x_k}. \tag{6.1}$$

We will consider the work done by the internal stresses in a virtual transition between two deformed states

$$\delta R dV = \frac{\partial \sigma_{ik}}{\partial x_h}\delta x_i dV = \frac{\partial \sigma_{ik}}{\partial x_k^0}\frac{|\lambda|}{\lambda_{kl}}\delta x_i dV_0.$$

Integrating the last relation, we find the work done by the internal stresses in a body with the initial volume V_0. We evaluate the intergral by parts, assuming that at the boundary of the region of integration the stresses disappear. We obtain

$$\int_V \delta R dV = -\int_{V_0}\sigma_{ik}\frac{|\lambda|}{\lambda_{hj}}\delta\lambda_{ij}dV_0 = \int_V \sigma_{ik}\frac{\delta\lambda_{ij}}{\lambda_{hj}}dV,$$

whence we find the work per unit of deformed volume

$$dR = -\frac{1}{2}\lambda_{ji}^{-1}\sigma_{ik}\lambda_{sk}^{-1}d\Lambda_{js}. \tag{6.2}$$

Using the known [7] equations for the change of internal and free energy in homogeneous deformation, together with (6.2), for a body with volume V we find

$$d\mathfrak{E} = TdS + \frac{V}{2}\lambda_{ji}^{-1}\sigma_{ik}\lambda_{sk}^{-1}d\Lambda_{js}; \tag{6.3}$$

$$d\mathfrak{F} = -SdT + \frac{V}{2}\lambda_{ji}^{-1}\sigma_{ik}\lambda_{sk}^{-1}d\Lambda_{js}. \tag{6.4}$$

From the latter relation we determine the elastic stress tensor $\sigma_{ik} = \frac{2}{V}\lambda_{kj}\lambda_{ls}\left(\frac{\partial\mathfrak{F}}{\partial\Lambda_{sj}}\right)_T$.

7. If, in addition to an infinitely large relaxation time, the system is also determined by other relaxation processes with relaxation times comparable with the time characterizing the motion, then the system will exhibit viscoelastic properties. We describe the motion of such a system by the method employed in section 5.

Using (6.3), we find the change of internal energy for unit mass

$$d\varepsilon = Tds + \frac{1}{\rho}dW + \frac{T}{\rho}X_\alpha d\xi^\alpha, \tag{7.1}$$

where $dW = \frac{1}{2}\lambda_{ij}^{-1}\sigma_{ik}{}^0\lambda_{sk}^{-1}d\Lambda_{js}$ is the change of elastic strain energy density; $\sigma_{ik}{}^0$ is the elastic stress tensor. Multiplying (7.1) by ρ, we find the change of internal energy density $dE = \rho Tds + \varepsilon d\rho + dW + TX_\alpha d\xi^\alpha$. Thus, the change of total energy per unit volume takes the form

$$\frac{dE}{dt} = \rho v_i \frac{\partial v_i}{\partial t} + \rho T\frac{ds}{dt} + \left(\varepsilon + \frac{v^2}{2}\right)\frac{d\rho}{dt} + \frac{\partial W}{\partial t} + TX_\alpha\frac{\partial\xi^\alpha}{\partial t}. \tag{7.2}$$

By analogy with the procedures described in sections 4 and 5, using Eqs. (3.1), (3.6), (3.7), and (7.1), we reduce Eq. (7.2) to the form

$$\frac{\partial E}{\partial t} + \frac{\partial}{\partial x_k}\left[\rho v_k\left(\varepsilon + \frac{v^2}{2}\right) - v_i\sigma_{ik} + TH_k\right] = T\sigma + \frac{dW}{dt} - \sigma_{ik}v_{ik} + H_i\nabla_iT + TX_\alpha\frac{d\xi_\alpha}{dt}. \tag{7.3}$$

Recalling the definition of the strain tensor, we obtain $\frac{d\Lambda_{ls}}{dt} = (\lambda_{qi}\lambda_{js} + \lambda_{qs}\lambda_{jl})v_{qj}$, after which we determine the rate of change of elastic energy density

$$\frac{dW}{dt} = \sigma_{(ik)}{}^0 v_{ik}. \tag{7.4}$$

We substitute the latter expression (7.3) and, on comparing the equation obtained with (3.3), obtain

$$Q_k = \rho v_k\left(\varepsilon + \frac{v^2}{2}\right) - v_i\sigma_{ik} + TH_k; \tag{7.5}$$

$$\sigma = (\sigma_{ik} - \sigma_{(ik)}{}^0)\frac{1}{T}v_{ik} - H_i\frac{1}{T}\nabla_iT - \frac{d\xi^\alpha}{dt}X_\alpha. \tag{7.6}$$

When $-p\delta_{ik}$ is substituted for $\sigma_{(ik)}{}^0$, the expression for the entropy production coincides with expression (5.3). If, as in section 5, we assume that the motion of the system is also determined by scalar and tensor parameters, then, obviously, with allowance for the above-mentioned substitution, all the subsequent results of section 5 are also applicable to the case considered here.

8. We have formulated the systems of equations of motion on the assumption that the state of the system is characterized by certain internal parameters, in terms of which the stress tensor was determined. Using the laws of variation of the internal variables with time, we can eliminate these variables from the stress tensor.

From Eqs. (5.7) and (5.9) we obtain

$$\xi'_{ik} = \alpha_{20}\int_0^\infty e^{-s/\tau}v'_{ik}(t-s)ds; \quad \xi = \mu_{10}\int_0^\infty e^{-s/\tau_1}v_{jj}(t-s)ds;$$

$$\xi_{jj} = \mu_{20}\int_0^\infty e^{-s/\tau_2}v_{jj}(t-s)ds. \tag{8.1}$$

whence we find the work per unit of deformed volume

$$dR = -\frac{1}{2}\lambda_{ji}^{-1}\sigma_{ik}\lambda_{sk}^{-1}d\Lambda_{js}.$$ (6.2)

Using the known [7] equations for the change of internal and free energy in homogeneous deformation, together with (6.2), for a body with volume V we find

$$d\mathfrak{E} = TdS + \frac{V}{2}\lambda_{ji}^{-1}\sigma_{ik}\lambda_{sk}^{-1}d\Lambda_{js};$$ (6.3)

$$d\mathfrak{F} = -SdT + \frac{V}{2}\lambda_{ji}^{-1}\sigma_{ik}\lambda_{sk}^{-1}d\Lambda_{js}.$$ (6.4)

From the latter relation we determine the elastic stress tensor $\sigma_{ik} = \frac{2}{V}\lambda_{kj}\lambda_{is}\left(\frac{\partial \mathfrak{F}}{\partial \Lambda_{sj}}\right)_T$.

7. If, in addition to an infinitely large relaxation time, the system is also determined by other relaxation processes with relaxation times comparable with the time characterizing the motion, then the system will exhibit viscoelastic properties. We describe the motion of such a system by the method employed in section 5.

Using (6.3), we find the change of internal energy for unit mass

$$d\varepsilon = Tds + \frac{1}{\rho}dW + \frac{T}{\rho}X_\alpha d\xi^\alpha,$$ (7.1)

where $dW = \frac{1}{2}\lambda_{ij}^{-1}\sigma_{ik}^0\lambda_{sk}^{-1}d\Lambda_{js}$ is the change of elastic strain energy density; σ_{ik}^0 is the elastic stress tensor. Multiplying (7.1) by ρ, we find the change of internal energy density $dE = \rho Tds + \varepsilon d\rho + dW + TX_\alpha d\xi^\alpha$. Thus, the change of total energy per unit volume takes the form

$$\frac{dE}{dt} = \rho v_i\frac{\partial v_i}{\partial t} + \rho T\frac{ds}{dt} + \left(\varepsilon + \frac{v^2}{2}\right)\frac{d\rho}{dt} + \frac{\partial W}{\partial t} + TX_\alpha\frac{\partial \xi^\alpha}{\partial t}.$$ (7.2)

By analogy with the procedures described in sections 4 and 5, using Eqs. (3.1), (3.6), (3.7), and (7.1), we reduce Eq. (7.2) to the form

$$\frac{\partial E}{\partial t} + \frac{\partial}{\partial x_k}\left[\rho v_k\left(\varepsilon + \frac{v^2}{2}\right) - v_i\sigma_{ik} + TH_k\right] = T\sigma + \frac{dW}{dt} - \sigma_{ik}v_{ik} + H_i\nabla_i T + TX_\alpha\frac{d\xi^\alpha}{dt}.$$ (7.3)

Recalling the definition of the strain tensor, we obtain $\frac{d\Lambda_{ls}}{dt} = (\lambda_{ql}\lambda_{js} + \lambda_{qs}\lambda_{jl})v_{qj}$, after which we determine the rate of change of elastic energy density

$$\frac{dW}{dt} = \sigma_{(ik)}^0 v_{ik}.$$ (7.4)

We substitute the latter expression (7.3) and, on comparing the equation obtained with (3.3), obtain

$$Q_k = \rho v_k\left(\varepsilon + \frac{v^2}{2}\right) - v_i\sigma_{ik} + TH_k;$$ (7.5)

$$\sigma = (\sigma_{ik} - \sigma_{(ik)}^0)\frac{1}{T}v_{ik} - H_i\frac{1}{T}\nabla_i T - \frac{d\xi^\alpha}{dt}X_\alpha.$$ (7.6)

When $-p\delta_{ik}$ is substituted for $\sigma_{(ik)}^0$, the expression for the entropy production coincides with expression (5.3). If, as in section 5, we assume that the motion of the system is also determined by scalar and tensor parameters, then, obviously, with allowance for the above-mentioned substitution, all the subsequent results of section 5 are also applicable to the case considered here.

8. We have formulated the systems of equations of motion on the assumption that the state of the system is characterized by certain internal parameters, in terms of which the stress tensor was determined. Using the laws of variation of the internal variables with time, we can eliminate these variables from the stress tensor.

From Eqs. (5.7) and (5.9) we obtain

$$\xi'_{ik} = \alpha_{20}\int_0^\infty e^{-s/\tau}v'_{ik}(t-s)\,ds; \quad \xi = \mu_{10}\int_0^\infty e^{-s/\tau_1}v_{jj}(t-s)\,ds;$$

$$\xi_{jj} = \mu_{20}\int_0^\infty e^{-s/\tau_2}v_{jj}(t-s)\,ds.$$ (8.1)

The velocity gradients in the integrands must be evaluated at the point where the "particle" is located at time t-s and, consequently, the integrals should be evaluated along the trajectories of the "particles." If the velocity gradients do not depend on the coordinates, the integration in (8.1) should be understood as integration with respect to time.

Substituting (8.1) in (5.6) and introducing the new notation $\alpha_{20}\alpha_{02}\beta_4 = h$, $\mu_{10}\omega_1 = z_1$, $\mu_{20}\omega_2 = z_2$, we obtain

$$\sigma_{ik}=\sigma_{ik}^0+2\eta v'_{(ik)}+2\int_0^\infty he^{-s/\tau}v'_{(ik)}(t-s)\,ds +\left[\zeta v_{jj}+\int_0^\infty (z_1e^{-s/\tau_1}+z_2e^{-s/\tau_2})v_{jj}(t-s)\,ds\right]\delta_{ik}. \tag{8.1}$$

For fluid systems $\sigma_{ik}^0 = -p\delta_{ik}$. The latter equation is also the governing equation of the system with scalar and tensor internal parameters for the class of motions with velocity gradients that do not depend on the coordinates. We note that, in general, the governing equation, understood as the relation between the stress tensor and the velocity gradient tensor, cannot be established for a given system in universal form, since, in accordance with (5.6), the tensor of the stresses at a given point depends not only on the value of the velocity gradient tensor but also on the values of the internal parameters, which are determined by the values of the velocity gradient tensor on the previous trajectory of that point.

Relation (8.2) can easily be extended to an arbitrary number of relaxation processes on the assumption that each process is associated with a normal coordinate. In this case the integrals in (8.2) contain sums, which for a large number of closely spaced relaxation times can be written in the integral form

$$\sum_i h_ie^{-s/\tau_i}=\int_0^\infty H(\tau)\tau^{-1}e^{-s/\tau}\,d\tau; \qquad \sum_i z_ie^{-s/\tau_i}=\int_0^\infty Z(\tau)\tau^{-1}e^{-s/\tau}\,d\tau.$$

By means of these relations we introduce the known [9] spectral functions $H(\tau)$ and $Z(\tau)$, which, of course, cannot be evaluated in the phenomenological theory. Finally, we write the linear governing equation in the following form

$$\sigma_{ik}=\sigma_{ik}^0+2\eta v'_{(ik)}+2\int_0^\infty\int_0^\infty H(\tau)\tau^{-1}e^{-s/\tau}v_{(ik)}(t-s)\,d\tau ds +\left[\zeta v_{jj}+\int_0^\infty\int_0^\infty Z(\tau)\tau^{-1}e^{-s/\tau}v_{jj}(t-s)\,d\tau ds\right]\delta_{ik}. \tag{8.3}$$

Thus, the idea of a relaxation spectrum can be introduced for the class of motions with a velocity gradient independent of the coordinates. For this type of motion the stress tensor is determined by the values of the velocity gradients at previous moments of time. For relaxation times that are small as compared with the period or characteristic time of the motion the behavior of the system is determined by the values of the gradients at moments of time close to the observation time t. Accordingly, the velocity gradients entering into the last relation can be expanded in powers of s near the time t and, consequently, the stress tensor will be determined by the velocity gradient and its higher time derivatives. In the zero-order approximation the relaxation processes make a contribution to the measured effective viscosity

$$\eta^*=\eta+\int_0^\infty H(\tau)\,d\tau; \qquad \zeta^*=\zeta+\int_0^\infty Z(\tau)\,d\tau. \tag{8.4}$$

In the next approximation the stress tensor is determined not only by the velocity gradients but also by the first-order accelerations.

9. As may be seen from a comparison of Eqs. (1.2) and (5.7), the linear theory of the motion of systems with internal parameters, considered in the previous sections, is insufficient to describe the motion of polymer systems. In fact, Eq. (1.2) can only be obtained from an equation for the "fluxes" quadratic in the "forces."

There is no great difficulty in writing down, instead of (5.6) and (5.9), expressions for the "fluxes" correct to terms of the second order in the gradients in general form (it must be assumed that in this case the stress tensor may be nonsymmetrical) and formulate the corresponding, naturally more clumsy, equations of motion, which will also be general equations of motion describing the motion of the systems considered in section 1. Moreover, in principle, for a given set of internal variables it is possible to formulate the equations of motion with any desired accuracy. Without dwelling on this, we will examine a possible variant of the nonlinear theory for the class of motions with velocities independent of the coordinates.

In the nonlinear case it is no longer possible to introduce relaxation times or, if they are introduced, they depend on the value of the internal variables. If the variables are not "entangled," the relaxation time depends only on its "own" coordinate $\tau_\alpha = \tau_\alpha(\xi^\alpha)$. If, however, the variables are "entangled," then the relaxation time will be determined, generally speaking, by the values of all the internal variables. For the case of scalar and tensor parameters in question

$$\tau = \tau(\xi, \xi_{jj}, \xi'_{ik}); \quad \tau_1 = \tau_1(\xi, \xi_{jj}, \xi'_{ik}); \quad \tau_2 = \tau_2(\xi, \xi_{jj}, \xi'_{ik}). \tag{9.1}$$

In the second approximation the relaxation times can be expressed in the form of linear functions of the variables.

As we have introduced relaxation times that depend on the internal variables for the class of motions with a velocity gradient independent of the coordinates in the case of a large number of internal variables, it is natural to introduce spectral functions of the relaxation times that likewise depend in explicit form on the values of the internal variables. Assuming that the viscosity term with $\tau = 0$ is included in the spectral function, we write the stress tensor in the following form:

$$\sigma_{ik}(\xi, \xi_{jj}, \xi'_{ik}) = \sigma_{ik}^0 + 2 \int_0^\infty \int_0^\infty H_{ikjl}(\tau, \xi, \xi_{jj}, \xi'_{ik}) \tau^{-1} e^{-s/\tau} v'_{jl}(t-s) \, d\tau ds + \int_0^\infty \int_0^\infty Z_{ik}(\tau, \xi, \xi_{jj}, \xi'_{ik}) \tau^{-1} e^{-s/\tau} v_{jj}(t-s) \, d\tau ds. \tag{9.2}$$

Naturally, if not all the internal variables are scalars, the spectral functions are tensors which at small velocity gradients, when the linear theory becomes applicable, go over into the linear spectral functions

$$H_{ikjl} \to \frac{1}{2} H(\tau) (\delta_{ij}\delta_{kl} + \delta_{il}\delta_{kj}); \quad Z_{ik} \to Z(\tau)\delta_{ik}.$$

As in the previous section, at small relaxation times the velocity gradients in (9.2) can be expanded in powers of s near the time t and, accordingly, in the zero-order approximation from (9.2) for an incompressible fluid we obtain the expression $\sigma_{ik} = -p\delta_{ik} + 2\eta_{ikjl} v_{jl}$, where we have introduced the effective coefficient of viscosity $\eta_{ikjl} = \int_0^\infty H_{ikjl}(\tau) \, d\tau$, which is a fourth-order tensor that depends on the internal parameters and, consequently, varies with the velocity gradient. As the velocity gradients tend to zero, $\eta_{ikjl} \to \frac{1}{2}\eta(\delta_{ij}\delta_{kl} + \delta_{il}\delta_{kj})$.

In the first approximation the coefficient of viscosity can be represented in a form linear in the internal parameters. Without writing down the general equations, we point out that for steady-state flow there follows from Eqs. (1.1) and (1.2) an expression for the viscosity coefficient tensor of a dilute polymer solution precisely in the form of a linear function of the internal parameters

$$\eta_{ikjl} = \eta(1 + 1.5\varphi)(\delta_{ij}\delta_{kl} + \delta_{il}\delta_{kj}) + \frac{1}{4}n\zeta \sum_\alpha (\langle \rho_k^\alpha \rho_i^\alpha \rangle \delta_{ij} + \langle \rho_l^\alpha \rho_i^\alpha \rangle \delta_{kj}).$$

Consequently, for this case the spectral function is also a fourth-order tensor. All the flow characteristics of dilute polymer solutions likewise reduce to the indicated viscosity anisotropy.

Apart from the tensor internal variables associated with the orientation and deformation of the coils, the flow of a concentrated polymer solution or melt is also determined by the scalar internal variables associated, for example, with a change in the equilibrium number of bonds [5]. These two groups of parameters — tensor and scalar — determine the two — orientational and structural — principal mechanisms of flow and, in particular, the gradient dependence of the viscosity of concentrated polymer systems. Taken separately, neither will lead to correct results.

SUMMARY

1. The motion of a viscoelastic system with m internal parameters is described by a system of $m + 5$ equations. The material constants of the system are the coefficients of the terms of the expansion of the "fluxes" in powers of the "gradients." The number and tensor order of the internal parameters determine properties of the viscoelastic system and also the number and physical significance of the material constants. From this standpoint viscoelastic systems can be classified according to rank — the tensor order of the internal parameters of the system — and order — the degree of the expansion of the "fluxes" in powers of the "gradients."

2. The behavioral characteristics of polymer solutions and melts are related with the presence of internal parameters — second-order tensors associated with the stretching and orientation of the macromolecules and scalars associated with changes in the structure of the system.

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