

RELAXATION THERMODYNAMICS AND VISCOELASTICITY OF ANISOTROPIC POLYMER SYSTEMS

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A theory of asymmetric viscoelasticity of anisotropic polymer systems has been formulated based on the relaxation dynamics of irreversible processes. Consideration has been given to the effect associated with the relaxation of couple stresses.

Introduction. Much attention has been given recently to studying the viscoelasticity of different anisotropic polymer systems. This is primarily true of polymer liquid crystals (LCs), cross-linked LC elastomers, polymer nanocomposites, and polymer suspensions. Their most significant difference from traditional polymer materials is the presence of relaxation anisotropy. The viscoelastic characteristics of anisotropic polymer media are tensor quantities. Therefore, unlike isotropic systems, they are determined by a substantially larger number of basic macroscopic parameters. Experimental determination of the tensor rheological properties of anisotropic polymer systems represents the most complicated problem. This field of rheology, on the whole, is only in the initial stage of development.

There can be two theoretical approaches to the rheology of anisotropic polymer systems. The first approach is based on molecular dynamics. It enables one to study the physical nature of anisotropic viscoelastic effects. The second, phenomenological, approach is restricted to studying only the macroscopic properties of these fairly complex polymer media. One is able, within the framework of this approach, to allow for the influence of the motion and strain of the microstructure of a medium on its rheological properties by introducing structural variables. The prime objective of continuum theories is the establishment of general constitutive equations under the minimum assumptions of the molecular structure of anisotropic media. Molecular theories are based on quite specific assumptions of the structure of these media and operate, unlike continuum theories, with a few molecular parameters.

The greatest progress toward description of the dynamics of low-molecular-weight LCs has been made at present using continuum theories [1–5]. An analogous situation is also observed in the theory of viscoelasticity of polymer LCs. The continuum theory of anisotropic viscoelasticity of LC polymers has been initiated by the investigations in [6–11]. A quasilinear rheological equation of state with anisotropic relaxation time and viscosity was formulated in them for simple reasons of symmetry. In this approach, an important role is played by the molecular flexibility of LC polymers and its associated elastic strains accompanying their flow. The anisotropic nonlinear viscoelasticity of polymer systems with different degrees of rigidity has begun to be studied in [12–16] within the framework of the classical thermodynamics of irreversible processes. This approach is based on the introduction of internal (latent) variables for description of viscoelastic effects. Here, critical is the fact that the physics of such continua can be described in general form by neither mechanics nor electro(magneto)dynamics separately. It is only the thermodynamics of irreversible processes that enables one to obtain a general description of the macroscopic properties of anisotropic polymer systems. Within the framework of a unified approach, one can investigate the anisotropic viscoelasticity of polymer liquids and rigid or highly elastic bodies, for example, LC elastomers [12, 15]. Nonequilibrium thermodynamics provides a general basis for description of the macroscopic properties of different anisotropic polymer systems in equilibrium and nonequilibrium situations.

In this work, we have presented a theory of anisotropic viscoelasticity of polymer nematics; the unit vector (director) characterizing microstructural orientation has been used as the structural variable in this theory. The rheological equations of state of irreversible processes have been derived based on their relaxation thermodynamics. This thermodynamic approach to the rheology of viscoelastic media is based on a natural generalization of the classical

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nonequilibrium thermodynamics created by Onsager, Prigogine, et al. [17, 18] to systems with a memory [19]. The simplest case, where thermodynamic fluxes and forces are related by relaxation equations of first order, has been considered.

Equations of Motion. Anisotropic polymer systems are of interest to researchers due to the unusual viscoelastic properties of these systems. From the macroscopic viewpoint, they are anisotropic viscoelastic media with internal rotations and asymmetric stresses. Regular description of their motion in terms of the velocity \mathbf{v} and the force-stress tensor $\underline{\underline{\sigma}}$ requires generalization. In this case, it is necessary to introduce an additional kinematic quantity $\underline{\underline{\Omega}}$, i.e., the angular velocity of internal rotation, which allows for reorientation of the molecules and their rotation about the intrinsic axes. This quantity should be understood as an averaged quantity characterizing the internal rotation, which differs from the rotation of the entire medium. In the dynamics of media with a free internal rotation, the angular velocity $\underline{\underline{\Omega}}$ is an independent quantity and does not depend on the angular rotational velocity of the entire medium $\underline{\underline{\omega}}$. Description of the motion of media with internal rotations is based on the equation for the change in the momentum [20]

$$\frac{d}{dt} \int_V \rho \mathbf{v} dv = \int_S \mathbf{t} ds + \int_V \rho \mathbf{f} dv \quad (1)$$

and the equation for the change in the total moment of momentum

$$\frac{d}{dt} \int_V \rho \mathbf{L} dv = \int_{\Sigma} (\mathbf{x} \times \mathbf{t} + \mathbf{c}) d\sigma + \int_V \rho (\mathbf{x} \times \mathbf{f} + \mathbf{m}) dv. \quad (2)$$

The density of the total moment of momentum \mathbf{L} is represented in the form

$$\mathbf{L} = \mathbf{x} \times \mathbf{v} + \mathbf{S}, \quad (3)$$

where $\mathbf{x} \times \mathbf{v}$ is the external moment of momentum and $\mathbf{S} = \underline{\underline{I}} \cdot \underline{\underline{\Omega}}$ is the internal moment of momentum per unit mass; $\underline{\underline{I}}$ for nematic (uniaxial) media is determined in the form

$$\underline{\underline{I}} = I_{\perp} \underline{\underline{\delta}} + (I_{\parallel} - I_{\perp}) \mathbf{nn}, \quad (4)$$

here \mathbf{n} is the orientation vector (director) of the medium and I_{\parallel} characterizes, on the average, the inertial properties of rotation of molecules about their intrinsic axes. Equations (1) and (2) represent Euler laws for a continuum; according to these laws, the rate of change of the momentum of its arbitrary volume V is determined by the sum of forces acting on it, whereas the rate of change of the total moment of momentum is determined by the sum of moments.

In the dynamics of continua, it is conventional to recognize two classes of forces and moments — bulk forces and moments \mathbf{f} and \mathbf{m} and surface ones \mathbf{t} and \mathbf{c} . The first quantities are single-valued-functions of the spatial points \mathbf{x} and the time t , whereas the second ones depend on the orientation \mathbf{l} of the area elements ds on which they act. It can be shown that they are linear functions of the orientation vector \mathbf{l} :

$$t_i = l_k \sigma_{ki}, \quad c_i = l_k \mu_{ki}. \quad (5)$$

These relations determine the tensors of force σ_{ij} and couple μ_{ij} stresses. The first subscript in them corresponds to the plane on which the stress acts, and the second subscript corresponds to the direction of its action. The diagonal components of the tensor μ_{ij} characterize torque moments, and the off-diagonal components characterize bending moments.

With account for (5), from the dynamic laws (1) and (2) we can obtain the following equations of motion in stresses:

$$\rho \frac{dv_i}{dt} = \sigma_{ji,j} + \rho f_i, \quad (6)$$

$$\rho \frac{dS_i}{dt} = \sigma_i + \mu_{ji,j} + \rho m_i, \quad \sigma_i = \varepsilon_{ijk} \sigma_{jk}. \quad (7)$$

The equation for internal rotation (7), which is called the moment equation, was obtained for the first time by the variational method by E. Cosserat and F. Cosserat in 1909 for solid deformable media [21]. It was later used to describe liquid media (in particular, LCs).

Thus, the stressed state of a continuum with internal rotations is characterized by two stress tensors σ and μ , which are asymmetric in the general case. The presence of asymmetric stresses leads to new types of flows. The effects associated with allowance for couple stresses are substantial in inhomogeneous flow fields. From Eq. (7) it follows that the asymmetry of the stress tensor σ is attributed to the presence of the couple stresses μ , the bulk moments \mathbf{m} , and the inertia of internal rotation. In the classical theory of continua, these asymmetry factors are absent; therefore, the stress tensor σ is symmetric. It is noteworthy that the inertial term related to the internal rotation in (7) is usually disregarded in the dynamics of low-molecular-weight nematics [22]. In viscoelastic (polymer) nematodynamics, it can turn out to be substantial at fairly long relaxation times of the medium by virtue of the interrelation of inertial and viscoelastic effects [11].

Constitutive Equations of Polymer Nematics. They are naturally derived based on the relaxation thermodynamics of irreversible processes. Let us use the well-known formula for the entropy production P_s in media with internal rotations and couple stresses:

$$TP_s = \sigma_{ij} \gamma_{ij} + \mu_{ij} \Omega_{j,i} - \left. \frac{df}{dt} \right|_T. \quad (8)$$

We will consider only isothermal processes and disregard thermal effects. According to the second law of thermodynamics, we have $P_s \geq 0$, i.e., the entropy production is strictly positive for nonequilibrium processes and disappears in equilibrium. The asymmetric strain-rate tensor γ_{ij} is determined in the form

$$\gamma_{ij} = e_{ij} + \omega_{ij}^r, \quad \omega_{ij}^r = \omega_{ij} - \omega_{ij}^{\text{in}}, \quad (9)$$

where $e_{ij} = v_{(j,i)}$ and $\omega_{ij} = v_{[j,i]}$. The internal rotation is characterized by the tensor $\omega_{ij}^{\text{in}} = \varepsilon_{ijk} \Omega_k$.

Experience shows that nematic LC media show orientational elasticity associated with the inhomogeneous director field $\mathbf{n}(\mathbf{x}, t)$. In pure form, it is found in a quiescent LC experiencing the moment action from the magnetic field or rigid boundaries [23]. Therefore, for the free energy of a polymer nematic and without allowance for the compressibility and thermal effects we take the following constitutive relation:

$$f = f(n_i, n_{i,j}). \quad (10)$$

Here we have used the same internal (structural) variables as in the case of low-molecular-weight LCs, i.e., the director and the director gradient $n_{i,j} = \partial n_i / \partial x_j$. An expression for the free energy of low-molecular-weight nematics was obtained by Oseen [24] and Frank [25]. In the region of small strains, one usually uses Frank's free energy for nematic media; it is determined as the quadratic form of orientational gradients:

$$2f = (K_1 - K_2) n_{i,j} n_{i,j} + K_2 n_{i,j} n_{i,j} + (K_3 - K_2) n_i n_j n_{k,i} n_{k,j}. \quad (11)$$

Based on (8) and (10), we can obtain expressions for thermodynamic forces and fluxes. We determine the material derivative of the free energy

$$\frac{df}{dt} = \frac{Df}{Dt} + \left(n_{[j} \frac{\partial f}{\partial n_{i]}} + n_{[j,k} \frac{\partial f}{\partial n_{i],k}} \right) \omega_{ij}, \quad (12)$$

where Df/Dt is the Jaumann free-energy derivative. By virtue of the rotational invariance of the free energy $df/dt = Df/Dt$, from expression (12) we obtain the following relation:

$$\varepsilon_{ijk} \left[n_j \frac{\partial f}{\partial n_k} + n_{j,m} \frac{\partial f}{\partial n_{k,m}} + n_{m,j} \frac{\partial f}{\partial n_{m,k}} \right] = 0. \quad (13)$$

In the equilibrium theory, it was derived for the first time by Eriksen [26]. Using this condition of invariance of the free energy to any rigid rotation of the medium and the relation

$$\frac{dn_i}{dt} = \varepsilon_{ijk} \Omega_j n_k, \quad \frac{d}{dt} n_{k,i} = \left(\frac{dn_k}{dt} \right)_i - n_{k,m} V_{m,i}, \quad (14)$$

we find the expression for the velocity of the free energy

$$\frac{df}{dt} = \frac{\partial f}{\partial n_i} \frac{dn_i}{dt} + \frac{\partial f}{\partial n_{i,j}} \frac{d}{dt} n_{i,j} = \sigma_{ik}^e \gamma_{ik} + \mu_{ki}^e \Omega_{i,k}. \quad (15)$$

Here we have introduced the following notation:

$$\sigma_{ij}^e = - \frac{\partial f}{\partial n_{k,i}} n_{k,j}, \quad \mu_{ij}^e = \varepsilon_{jmk} n_m \frac{\partial f}{\partial n_{k,i}} \quad (16)$$

for nondissipative tensors of force and couple stresses. With account for (15), the expression for the entropy production (8) is written in the form

$$TP_s = \tilde{\sigma}_{ij} \gamma_{ij} + \tilde{\mu}_{ij} \Omega_{j,i} \geq 0, \quad (17)$$

where $\tilde{\underline{\sigma}}$ and $\tilde{\underline{\mu}}$ are the dissipative contributions to the force and couple stresses. The total stresses are determined in the form

$$\sigma_{ij} = -p \delta_{ij} + \sigma_{ij}^e + \tilde{\sigma}_{ij}, \quad \mu_{ij} = \mu_{ij}^e + \tilde{\mu}_{ij}. \quad (18)$$

In most cases, polymer nematics can be considered as incompressible media. The first equation in (18) determines the total stress for liquids with a constant density accurate to the arbitrary additive isotropic tensor.

Let us select γ_{ij} and $\Omega_{j,i}$ as the forces and the quantities $\tilde{\sigma}_{ij}$ and $\tilde{\mu}_{ij}$ conjugate to them as the fluxes. For anisotropic media whose flow is accompanied by relaxation processes it is natural to assume that the relationship between the forces and fluxes in the simplest case is determined, without allowance for the cross effects, by the relaxation equations of first order

$$\tau_{ijkm} \frac{D}{Dt} \tilde{\sigma}_{km} + \tilde{\sigma}_{ij} = \eta_{ijkm} \gamma_{km}, \quad (19)$$

$$\Theta_{ijkm} \frac{D}{Dt} \tilde{\mu}_{km} + \tilde{\mu}_{ij} = \beta_{ijkm} \Omega_{m,k}. \quad (20)$$

In what follows, we will use only the Jaumann definition of the rate of change of stresses $Da_{ij}/dt = \dot{a}_{ij} + a_{ie} \omega_{ej} - \omega_{ie} a_{ej}$. Other definitions of the rate of change of asymmetric stresses contain additional terms which are more conveniently introduced into the constitutive equations [10]. The nonnegative character of the entropy production (17) imposes additional restrictions on the material parameters determined by the rheological equations (19) and (20). In them, τ and Θ are the relaxation-time tensors and $\underline{\eta}$ and $\underline{\beta}$ are the corresponding viscosity tensors determined by the specific properties of the media.

For nematic media these tensors must satisfy the transversal-isotropy condition associated with the presence of preferred orientation and be even functions of the director, since the unit vector \mathbf{n} is physically indistinguishable from

–**n**. Such restrictions substantially decrease the number of independent material parameters determined by these tensors. In the case of an incompressible liquid, the nematic viscosity is determined in the form of the sum [10]

$$\eta_{ijklm} = \alpha_{ijklm}^0 + \alpha_{ijklm}^1 \quad (21)$$

of the isotropic tensor

$$\alpha_{ijklm}^0 = \eta_1 \delta_{ik} \delta_{jm} + \eta_2 \delta_{im} \delta_{jk}$$

and the anisotropic fourth-rank tensor

$$\alpha_{ijklm}^1 = \eta_3 n_{ijkm} + \eta_4 n_{ik} \delta_{jm} + \eta_5 n_{jk} \delta_{im} + \eta_6 n_{im} \delta_{jk} + \eta_7 n_{jm} \delta_{ik},$$

where we have introduced the following notation: $n_{ij} = n_i n_j$ and $n_{ijke} = n_i n_j n_k n_e$. The nematic viscosity tensor with account for spin effects is characterized by seven scalar coefficients of viscosity η_α . The nematic tensors of relaxation times τ and Θ and the moment viscosity β have an analogous structure but with other scalar coefficients.

The rheological equation (19) was obtained for the first time in [10] for simple reasons of symmetry. If we disregard the inertia of internal rotation, the bulk moments, and the couple stresses, it is reduced to the rheological equation of an anisotropic viscoelastic liquid with a symmetric stress tensor (obtained in [6]). The class of liquids determined by this equation is characterized by three basis coefficients of viscosity and three basis relaxation times.

In the particular case, where $\Theta = 0$, the rheological equation (20) determines the viscous couple stress for incompressible nematics

$$\tilde{\mu}_{ij} = \beta_1 \Omega_{i,j} + \beta_2 \Omega_{j,i} + \beta_3 \Omega_{i,k} n_{kj} + \beta_4 \Omega_{j,k} n_{ki} + \beta_5 \Omega_{k,i} n_{kj} + \beta_6 \Omega_{k,j} n_{ki} + \beta_7 \Omega_{k,n} n_{knij}. \quad (22)$$

If we disregard the inertia of internal rotation ($I = 0$), the relaxation (polymer) properties of a medium ($\tau = 0$), and the dynamic contribution to couple stresses ($\tilde{\mu} = 0$), the constitutive equations (19)–(21) are reduced to the rheological equation of Leslie–Ericksen theory for low-molecular-weight LCs [27, 28].

Orientational Dynamics. The dynamics of the director **n** appearing in the rheological equations of polymer nematics is described using an additional equation which is characterized by the orientational properties of a medium. This equation can be derived directly from the equation for internal motion (7). As a result, we obtain the equation for the director [11]

$$\rho I_{ij}^\perp \frac{d^2 n_j}{dt^2} - \rho I_{\parallel} \Omega_{\parallel} \Omega_i^\perp = h_i^\perp + 2n_j \tilde{\sigma}_{ji}^a \quad (23)$$

and the spin equation

$$\rho I_{\parallel} \frac{d\Omega_{\parallel}}{dt} = \varepsilon_{ijk} n_i \tilde{\sigma}_{jk}^a, \quad (24)$$

which allow for three rotational degrees of freedom. The first equation describes the reorientation of the director, and the second one describes the rotational degree of freedom associated with the rotation of molecules about their intrinsic axes. The angular velocity of internal rotation $\Omega = \Omega_{\parallel} + \Omega_{\perp}^{\perp}$ is made up of the rotational velocity of the director $\Omega_i^{\perp} = \varepsilon_{ijk} n_j dn_k / dt$ and the velocity of internal rotation about the director $\Omega_i^{\parallel} = \Omega_{\parallel} n_i$, where $\Omega_{\parallel} = \Omega_{\parallel} n_i$. In the equations of rotational motion (23) and (24), $I_{\perp}^{\perp} = I_{\perp} \delta^{\perp}$ is the transverse component of the rotational-inertia tensor, $\mathbf{h}^{\perp} = \mathbf{h} \delta^{\perp}$ is the transverse component of the molecular field, and $\delta^{\perp} = \delta - \mathbf{nn}$ is the transverse Kronecker symbol.

The internal elastic forces of an LC nematic and the external forces acting on the director from the magnetic field can be described using a unified molecular field $\mathbf{h} = \mathbf{h}^e + \mathbf{h}^m$. Here \mathbf{h}^e plays the role of a molecular field tending to establish the same direction of the director in the entire volume of the nematic. According to [3], it is determined in the form

$$h_i^e = \pi_{ijj} - \partial f / \partial n_i, \quad \pi_{ij} = \partial f / \partial n_{j,i}. \quad (25)$$

The presence of the magnetic field leads to an additional contribution to the molecular field:

$$h_i^m = \chi_a n_j H_j H_i. \quad (26)$$

Here $\chi_a = \chi_{\parallel} + \chi_{\perp}$ and χ_{\parallel} and χ_{\perp} are the principal values of the dynamic-susceptibility tensor along the director and across it respectively. It is assumed that the magnetic field influences the stress tensor only in terms of the change in the orientation. Therefore, the magnetic-field strength \mathbf{H} as an independent variable does not appear in the free energy.

In deriving Eqs. (23) and (24), we have allowed only for the equilibrium contribution to couple stresses, which, according to (16), is determined in the form $\mu_{mi} = \varepsilon_{ijk} n_j \pi_{mk}$. Here we do not consider the effects associated with inhomogeneous internal rotations; therefore, the dynamic contribution to couple stresses is equal to zero. In this case, we have the relation

$$\varepsilon_{ijk} \partial \mu_{mk} / \partial x_m = -2\sigma_{ij}^{ea} + n_i h_j^{\perp} - h_i^{\perp} n_j, \quad (27)$$

where $\sigma_{ij}^{e,a}$ is the asymmetric part of the nondissipative stress tensor. The above relation has been used in deriving Eqs. (23) and (24).

Thus, orientational and spin dynamics is determined by the asymmetric stresses $\tilde{\sigma}^a$, which in turn are described, according to (19), by the system of interrelated relaxation equations

$$\begin{aligned} \tau_{[ij][km]} \frac{D\tilde{\sigma}_{km}^a}{Dt} + \tau_{[ij](km)} \frac{D\tilde{\sigma}_{km}^s}{Dt} + \tilde{\sigma}_{ij}^a &= \eta_{[ij](km)} e_{km} + \eta_{[ij][km]} \omega_{km}^r, \\ \tau_{(ij)(km)} \frac{D\tilde{\sigma}_{km}^s}{Dt} + \tau_{(ij)[km]} \frac{D\tilde{\sigma}_{km}^a}{Dt} + \tilde{\sigma}_{ij}^s &= \eta_{(ij)(km)} e_{km} + \eta_{(ij)[km]} \omega_{km}^r, \end{aligned} \quad (28)$$

where $\tilde{\sigma}^s$ is the symmetric part of the stress tensor. Here symmetrization is by the subscripts in parentheses, whereas square brackets denote asymmetrization by the corresponding subscripts. An analysis of Eqs. (23)–(28) shows that inertial and viscoelastic effects can be related in the orientational dynamics of viscoelastic anisotropic media at long relaxation times.

Let us consider the simple case where the magnetic field is absent and the inertia of internal rotation and the orientational elasticity can be disregarded. Under these conditions, we have $\tilde{\sigma}^a = 0$ according to (23). With allowance for this, from system (28) we obtain the following orientation equation for viscoelastic (polymer) nematics:

$$\tau_{im} \frac{D^2 n_m}{Dt^2} + \frac{Dn_i}{Dt} = b_{ijm} \left(\lambda_1 \theta^* \frac{De_{jm}}{Dt} + \lambda_2 e_{jm} \right), \quad (29)$$

where $\tau_{ij} = \theta^* \delta_{ij}^{\perp}$ and $b_{ijk} = \delta_{ij}^{\perp} n_k$. In deriving (29), we have used the relation $Dn_i/Dt = \omega_{ij}^r n_j$, where $Dn_i/dt = dn_i/dt - \omega_{ij}^r n_j$ is the Jaumann derivative of the director.

Thus, the evolution equation for the director of polymer nematics (29) is viscoelastic in character. It was obtained for the first time in [16] based on the traditional thermodynamic approach to the rheology of viscoelastic media. In this case, one is able to consider Maxwell-type viscoelastic nematodynamics within the framework of the thermodynamics of irreversible processes by extending the notion of the system's state. Two additional (latent) variables — the tensors of elastic strain and relative elastic rotation — are introduced into the free energy. In the case of viscous nematodynamics, the equation for the director (29) is reduced to the well-known orientation equation of Ericksen

$$\frac{Dn_i}{Dt} = \lambda (e_{ij} n_j - n_i n_j n_k e_{jk}), \quad (30)$$

here λ is the dimensionless material parameter determining the character of the orientational process.

The orientational relaxation of LC polymers has experimentally been studied in [19, 30] and a substantial growth in the relaxation time of the director of nematic comb-shaped polymers as compared to low-molecular-weight systems has been found.

Conclusions. The investigation carried out is primarily aimed at forming a general approach to description of the viscoelasticity of different anisotropic polymer systems. They are considered as anisotropic viscoelastic media with internal rotations and asymmetric stresses. The concept of internal rotation provides a unified basis for studying the macroscopic behavior of solid and liquid anisotropic polymer media. In the present work, we have derived the rheological equations of state and the equation of orientation of nematic (uniaxial) viscoelastic liquids based on the relaxation dynamics of irreversible processes. These equations are viscoelastic (relaxation) in character and determine a new class of anisotropic viscoelastic liquids.

From the molecular viewpoint, the low- and high-frequency viscoelasticity of polymer systems is determined from the dynamic equations of macromolecules with a memory which allow for the relaxation interaction of the macromolecules with their viscoelastic environment [31, 32]. These generalized Langevin equations are derived from microscopic equations of motion [33, 34]. Such an approach, which is based on non-Markovian equations of motion of individual molecules, provides an explanation for the high-frequency viscoelasticity of ordinary (low-molecular-weight) liquids [35]. Critical is the fact that this approach describes the general molecular mechanism of viscoelasticity of all liquids.

The considered thermodynamic approach to the rheology of polymer liquids makes it possible to investigate viscoelastic phenomena without using an additional parameter, which is usually assigned the meaning of elastic strain. Here we have considered the simplest case, where the thermodynamic forces and fluxes are related by the quasilinear relaxation equation of first order. All the kinematic variables have been selected without reference to the rheological properties of the viscoelastic liquids considered.

The thermodynamic theory of viscoelastic nematodynamics proposed allows a simple generalization to polydisperse systems characterized by the anisotropic spectrum of relaxation times. It is noteworthy that, extending the understanding of the system's state by introducing additional variables, we can, in principal, formulate the constitutive equations of polydisperse media so that they contain only the quantities referring to a single spatial point at a single instant of time. However, the additional objective — the necessity of solving a system of ordinary differential equations describing the simultaneous relaxation of a large number of internal parameters — arises in this traditional thermodynamic approach to viscoelasticity, which is based on the principle of time localizability.

NOTATION

\mathbf{c} , surface moment; d/dt , material derivative; D/Dt , Jaumann derivative; e_{ij} , symmetric part of the velocity gradient; \mathbf{f} , bulk force; f , free energy; \mathbf{h} , molecular field; \mathbf{h}^e , elastic part of the molecular field; \mathbf{h}^m , magnetic part of the molecular field; \mathbf{h}^\perp , transverse component of the molecular field; \mathbf{H} , magnetic-field strength; $\underline{\underline{I}}$, rotational-inertia tensor; I_\parallel and I_\perp , principal values of the inertia tensor; K_α , Frank modulus; \mathbf{L} , total moment of momentum; \mathbf{l} , unit vector of the external normal to S ; \mathbf{m} , bulk moment; n_i , director; $n_{i,j}$, director gradient; P_s , entropy production; p , isotropic pressure; \mathbf{S} , internal moment of momentum; T , temperature; \mathbf{t} , surface force; t , time; V , selected volume of the medium; \mathbf{v} , velocity of translational motion of the medium's element; \mathbf{x} , radius vector of a point of the medium; β_α , coefficient of moment viscosity; $\underline{\underline{\beta}}$, moment-viscosity tensor; γ_{ij} , asymmetric strain-rate tensor; δ , unit tensor; δ^\perp , transverse Kronecker symbol; η_α , coefficient of viscosity; $\underline{\underline{\eta}}$, viscosity tensor; θ^* , orientational relaxation time; Θ , tensor of moment relaxation times; $\underline{\underline{\mu}}$, couple-stress tensor; $\underline{\underline{\mu}}_{ij}^e$, nondissipative contribution to the couple stresses; $\underline{\underline{\mu}}_{ij}$, dissipative contribution to the couple stresses; ρ , density of the medium; $\underline{\underline{\sigma}}$, force tensor; $\underline{\underline{\sigma}}_{ij}^e$, nondissipative stress tensor; $\underline{\underline{\sigma}}_{ij}^{ea}$, asymmetric part of the tensor $\underline{\underline{\sigma}}_{ij}^e$; $\underline{\underline{\sigma}}_{ij}$, dissipative stress tensor; $\underline{\underline{\sigma}}_{ij}^{se}$ and $\underline{\underline{\sigma}}_{ij}^{sa}$, symmetric and asymmetric parts of the tensor $\underline{\underline{\sigma}}_{ij}$; Σ , surface bounding the medium's volume; τ , relaxation-time tensor; χ_\parallel and χ_\perp , principal values of the dynamic-susceptibility tensor; λ , λ_1 , and λ_2 , dimensionless material parameters; $\underline{\underline{\Omega}}_i$, angular velocity of internal rotation; $\underline{\underline{\Omega}}_i^\perp$, rotational velocity of the director; $\underline{\underline{\Omega}}_i^\parallel$, velocity of internal rotation about the director; $\underline{\underline{\Omega}}_{i,j}$, gradient of the angular velocity of internal rotation; ω_{ij} , asymmetric part of the velocity gradient; ω_{ij}^{in} , internal-rotation tensor. Subscripts and superscripts: a, asymmetric; e, equilibrium, in, internal; m, magnetic; r, relative; s, symmetric.

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