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RHEOLOGY OF LIQUID-CRYSTALLINE POLYMERIC SYSTEMS

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Based on the Zubarev method of nonequilibrium distribution functions, a statistical-mechanical theory of the rheological properties of liquid-crystalline polymers has been constructed. The distinctive features of the media in question in the case of shear flow have been described using this theory.

Both experimental and theoretical investigations of the rheological properties of liquid-crystalline polymeric systems have become more active in the last decade [1]. It was found that the flow of these systems differs significantly from the flow of isotropic polymers. In particular, in the case of steady-state shear flow of liquid-crystalline polymeric systems the difference between the diagonal elements of the tensor of stresses streamwise and across the flow (the so-called first difference of normal stresses) is nonzero and depends on the rate of shear deformation. However, attempts at constructing the rheology of liquid-crystalline polymeric systems within the theory of low-molecular-weight liquid crystals showed the inability of the latter to adequately describe the flow of the media in question, which led to the necessity of generalizing the equations of hydrodynamics of liquid crystals to the case of polymeric systems. In the majority of works, use is made of the phenomenological approach in which the rheological characteristics of a medium are found experimentally while the structural parameters have no explicit microscopic determination [2].

In this connection, the problem of construction of a statistical-mechanical theory of the rheological properties of liquid-crystalline polymeric systems is pressing. The formulated problem will be solved based on the general methods of modern nonequilibrium statistical mechanics [3] with the use of the description of the liquid-crystalline polymeric system as a system with a variable internal structure. As the parameters of state of the medium we select the average values of the microscopic densities of mass, momentum, and energy

$$\hat{\rho}\,(\mathbf{x}, t)\ \sum_{\nu=1}^{N} m\delta\,(\mathbf{x}^{\nu}\,(t) - \mathbf{x})\,, \tag{1}$$

$$\hat{\mathbf{p}}\,(\mathbf{x}, t)\ \sum_{\nu=1}^{N} m\mathbf{v}^{\nu}\delta\,(\mathbf{x}^{\nu}\,(t) - \mathbf{x})\,, \tag{2}$$

$$\hat{H}\,(\mathbf{x}, t)\ \sum_{\nu=1}^{N} H_{\nu}\delta\,(\mathbf{x}^{\nu}\,(t) - \mathbf{x})\,, \tag{3}$$

the energy of an individual molecule

$$H_{\nu} = \frac{1}{2}\left(\frac{(P^{\nu})^{2}}{m} + \sum_{\alpha=1}^{n} \frac{(\pi^{\alpha\nu})^{2}}{m_{\alpha\nu}} + \sum_{\alpha,\beta,\mu} \Phi\,(\mathbf{R}^{\alpha\nu}, \mathbf{R}^{\beta\mu})\right) \tag{4}$$

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is expressed in terms of its translational momentum $\mathbf{P}^{\nu} = m\mathbf{v}^{\nu}$ and in terms of the momentum $\pi^{\alpha\nu}$ which is canonically conjugate to the radius vector $\mathbf{y}^{\alpha\nu}$ of the particle α of mass $m_{\alpha\nu}$; the radius vector is reckoned from the center of mass of the molecule with a number ν whose position is prescribed by the radius vector $\mathbf{x}^{\nu}$.

The interaction between the particles α and β is described by the potential $\Phi(\mathbf{R}^{\alpha\nu}, \mathbf{R}^{\beta\mu})$, which depends on their arrangement characterized by the radius vectors $\mathbf{R}^{\alpha\nu} = \mathbf{x}^{\nu} + \mathbf{y}^{\alpha\nu}$ and $\mathbf{R}^{\beta\mu} = \mathbf{x}^{\mu} + \mathbf{y}^{\beta\mu}$.

To allow for the variable internal structure we use the density of the moment of inertia of the molecule (of the structural unit)

$$\hat{J}_{ij}(\mathbf{x}, t) = \sum_{\nu=1}^{N} \left(\sum_{\alpha=1}^{n} m_{\alpha\nu} y_i^{\alpha\nu} y_j^{\alpha\nu} \right) \delta(\mathbf{x}^{\nu} - \mathbf{x}) \tag{5}$$

and its generalized moment of momentum [3]

$$\hat{P}_{ij}(\mathbf{x}, t) = \sum_{\nu=1}^{N} \left(\sum_{\alpha=1}^{n} \pi_i^{\alpha\nu} y_j^{\alpha\nu} \right) \delta(\mathbf{x}^{\nu} - \mathbf{x}) \, . \tag{6}$$

The quantity $\hat{P}_{ij}(\mathbf{x}, t)$ yields simultaneous description of the rotation of the structural unit and the rate of distortion of its shape. The antisymmetric part of the quantity $\hat{P}_{ij}(\mathbf{x}, t)$ is the intrinsic moment of momentum

$$\hat{L}_i(\mathbf{x}, t) = -\, e_{ikn} \hat{P}_{kn}(\mathbf{x}, t) \, , \tag{7}$$

while its symmetric part determined by the equality

$$\hat{L}_{ik}(\mathbf{x}, t) = 2^{-1} (\hat{P}_{ik} + \hat{P}_{ki}) \, , \tag{8}$$

characterizes the rate of change of the molecular shape.

The equations of motion of the introduced dynamic quantities are obtained using the formalism of Poisson brackets and they are represented in the form

$$\begin{gathered}
\frac{\partial \hat{\rho}(x, t)}{\partial t} = -\frac{\partial \hat{p}_k(x, t)}{\partial x_k} \, , \quad \frac{\partial \hat{p}_i(x, t)}{\partial t} = \frac{\partial \hat{\tau}_{ik}}{\partial x_k} \, , \\
\frac{\partial \hat{H}(x, t)}{\partial t} = -\frac{\partial \hat{j}_k^{H}(x, t)}{\partial x_k} \, , \quad \frac{\partial \hat{J}_{ij}(x, t)}{\partial t} = 2\hat{L}_{ij}(x, t) - \frac{\partial \hat{j}^{J}_{ijl}}{\partial x_k} \, , \\
\frac{\partial \hat{L}_{ik}(x, t)}{\partial t} = \hat{t}_{ik} + \frac{\partial \hat{t}_{ikl}}{\partial x_l} \, , \quad \frac{\partial \hat{L}_i(x, t)}{\partial t} = \frac{\partial \hat{\pi}_{ik}}{\partial x_k} + l_{ikl} \hat{\tau}_{lk} \, .
\end{gathered} \tag{9}$$

The expressions for the corresponding microscopic flows and sources are given in [3]. In what follows, we will disregard the inertia of deformation of a molecule which can manifest itself at high frequencies close to the frequencies of intramolecular vibrations; therefore, we exclude the equations of motion for $\hat{L}_{ik}$ from consideration.

Before the averaging of microscopic equations of motion it is necessary to change to the co-moving reference system [3]. Co-motion is carried out by the average values of the velocity of macroscopic motion of the medium $\mathbf{v}(\mathbf{x}, t)$, the angular velocity of rotation of the structural elements $\omega(\mathbf{x}, t)$, and the average rate of deformation of the structural element $\varphi_{ij}(\mathbf{x}, t)$. The indicated characteristics of macroscopic motion of the medium with a variable internal structure are determined by the relations

$$\langle \hat{p}_i(x, t) \rangle = \langle \hat{\rho}(x, t) \rangle_q \, v_i(x, t) \, , \quad \langle \hat{L}_i(x, t) \rangle_q = \langle \hat{I}_{ik}(x, t) \rangle_q \, \omega_k(x, t) \, ,$$

$$\langle \hat{p}_{ik}(x, t)\rangle_q = \langle \hat{J}_{lk}(x)\rangle_q \, \Phi_{il}(x, t) \,, \tag{10}$$

the tensor $\Phi_{il}(x, t)$ describes simultaneously the rotation of the structural element and its deformation

$$\Phi_{ik} = - e_{ikm}\omega_m + \varphi_{ik} \,, \quad \varphi_{ik} = 2^{-1}(\Phi_{ik} + \Phi_{ki}) \,, \tag{11}$$

while the angle brackets with a subscript q denote quasiequilibrium averaging,

$$\langle \hat{I}_{ik}(x, t)\rangle_q = \langle \hat{J}_{ik}\rangle_q - \langle \hat{J}_{nn}\rangle_q \, \delta_{ik} \tag{12}$$

is the density of the moment of inertia.

It is of interest to note that the quasiequilibrium averaging of the equation of motion for the generalized moment of momentum leads to equations which are a generalization of the Eulerian equations of the dynamics of rotation of a solid body to the case where the body is capable of being deformed [3].

The total nonequilibrium averaging of the equations of motion for the microscopic densities mentioned is carried out using the Zubarev distribution function [4] (which is the solution of the Liouville equation at the level of contracted description of flow of the medium under study) with the application of the average values of the densities of dynamic quantities used. The result of the averaging has the form [3]

$$\frac{\partial \rho}{\partial t} = - \frac{\partial \rho v_i}{\partial x_i} \,, \quad \rho \frac{\partial v_i}{\partial t} = - \rho v_k \frac{\partial v_i}{\partial x_k} - \frac{\partial \tau_{ik}}{\partial x_k} \,, \qquad \frac{\partial J_{ij}}{\partial t} = 2L_{ij}(x, t) + j_{ij} \,, \quad \frac{\partial L_i}{\partial t} = \frac{\partial \pi_{ik}}{\partial x} + e_{ikl}\tau_{lk} \,. \tag{13}$$

Here $\tau_{ik} = \langle \hat{\tau}_{ik}\rangle$, $j_{ik} = \langle 2(\hat{L}_{ik} - \langle \hat{L}_{ik}\rangle_q) - \partial \hat{j}^{I}_{ikl}/\partial x_l\rangle$, $L_{ij} = \langle \hat{L}_{ij}\rangle_q$, $L_i = \langle \hat{L}_i\rangle$, and $J_{ij} = \langle \hat{J}_{ij}\rangle$; $q_i = \langle \hat{j}^{H}_i\rangle$ is the heat flux; the angle brackets denote nonequilibrium averaging.

We note that the quasiequilibrium averaging results in the following rigorous expressions for L_i and L_{ik}:

$$L_m = I_{mk}\omega_k + 2^{-1}e_{mki}(J_{kj}\varphi_{ij} - J_{ij}\varphi_{kj}) \,, \quad L_{ik} = 2^{-1}\omega_l(e_{ilj}J_{kj} + e_{klj}J_{ij}) + 2^{-1}(J_{kj}\varphi_{ij} + J_{ij}\varphi_{kj}) \,. \tag{14}$$

This yields an important conclusion on the interrelation between the macroscopic rotation of the structural unit and its deformation.

The fundamental result of the nonequilibrium averaging is not only the derivation of macroscopic equations of motion but also the obtaining of material equations (rheological relations). Finally, a closed system of macroscopic equations of motion and rheological relations is established. In the case in question the material equations have the form

$$\begin{gathered} \tau_{ik} = - P\delta_{ik} + \beta L^{\tau,\tau}_{ikmn}e_{mn} - L^{\tau,j}_{ikmn}\lambda_{mn} \,, \quad j_{ik} = \beta L^{j,\tau}_{ikmn}e_{mn} - L^{j,j}_{ikmn}\lambda_{mn} \,, \\ \pi_{ik} = \overset{0}{\pi}_{ik} + L^{\pi,q}_{ikl}\frac{\partial \beta}{\partial x_l} + \beta L^{\pi,\pi}_{ikmn}\frac{\partial \omega_m}{\partial x_n} \,, \quad q_i = L^{q,q}_{ik}\frac{\partial \beta}{\partial x_k} + \beta L^{\pi,\pi}_{ikmn}\frac{\partial \omega_m}{\partial x_n} \,, \end{gathered} \tag{15}$$

$L^{n,m}$ are the corresponding tensors of kinetic coefficients. The superscripts denote the fluxes whose time correlation determines the corresponding kinetic coefficient, i.e.,

$$L^{n,m} = \int d\mathbf{x}' \int_{-\infty}^{0} dt' e^{\varepsilon t'} \langle \hat{j}^{n}(\mathbf{x}) \exp[(1 - \Pi_{\mathrm{M}}) Lt'] \hat{j}^{m}(\mathbf{x}')\rangle_0 \,. \tag{16}$$

where Π_{M} is the Mori projection operator [3] and L is the Liouville operator.

The thermodynamic parameter λ_{mn} is expressed in the form of the functional derivative of the Helmholtz free energy with respect to the density of the moment of inertia:

$$\lambda_{mn} = \frac{\delta F}{\delta J_{mn}} \,. \tag{17}$$

Similarly to how the angular velocity of proper rotation of molecules relaxes to the angular velocity $\Omega = 2^{-1}$ rot $\mathbf{v}$ of hydrodynamic rotation, the tensor of internal deformation of the structural element relaxes to the tensor of deformation rates $2^{-1}(v_{i,k} + v_{k,i})$. Upon completion of the relaxation mentioned, we have $\Phi_{ik} = v_{i,k}$. In what follows, we will consider the indicated relaxed states.

With allowance for the above remarks, we write, in explicit form, the equation for the evolution of the structural parameter J_{ij} and the material equation for the stress tensor τ_{ik}:

$$\frac{\partial J_{ij}}{\partial t} = - J_{ij} v_{k,k} + J_{jn} v_{i,n} + J_{in} v_{j,n} - L^{j,j}_{ijmn} \lambda_{mn} + \beta L^{j,\tau}_{ijmn} v_{mn} \,, \tag{18}$$

$$\tau_{ik} = - P\delta_{ik} + \beta L^{\tau,\tau}_{ikmn} v_{m,n} - L^{\tau,j}_{ikmn} \lambda_{mn} \,. \tag{19}$$

Here $v_{i,n} = \partial v_i / \partial x_n$ are the gradients of the velocity of hydrodynamic flow in spatial coordinates.

In describing the rheological properties of the liquid-crystalline polymeric system, we should allow for the processes of retardation. To do this we will consider the tensor of kinetic coefficients

$$L^{\tau,\tau}_{ikmn}(t - t') = \int d\,\mathbf{x}' \int_{-\infty}^{0} dt' \exp(\varepsilon t') \, \langle \hat{\tau}_{ik}(\mathbf{x}, t) \exp[(1 - \text{Ï}_{\text{ĵ}}) L t'] \, \hat{\tau}_{mn}(\mathbf{x}', t') \rangle_0 \tag{20}$$

as the integral operator. Then the contribution to the stress tensor (19) related to the deformation-rate field will be written in the form [3]

$$\tau'_{ik} = L^{\tau,\tau}_{ikmn} v_{m,n} = \int d\,\mathbf{x}' \int_{-\infty}^{0} dt' \exp(\varepsilon t') \, \langle \hat{\tau}_{ik}(\mathbf{x}, t) \exp[(1 - \text{Ï}_{\text{ĵ}}) L t'] \, \hat{\tau}_{mn}(\mathbf{x}', t') \rangle_0 \, v_{m,n}(\mathbf{x}, t') \,. \tag{21}$$

In what follows, we will model the integral kernel in the last equality in the form of the exponent $\lambda^{-1} a'_{ikmn}$ exp $[-\lambda^{-1}(t - t')]$, assuming (for the sake of simplicity) the existence of just a single time λ of relaxation, which enables us to obtain the formula

$$\tau'_{ik} + \lambda \frac{d\tau'_{ik}}{dt} = \beta a'_{ikmn} e_{mn} \,, \tag{22}$$

relating the tensor τ'_{ik} determined by formula (21) to its time derivative.

In considering the viscous properties of low-molecular-weight liquid crystals, one usually disregards the contributions of retardation processes; then the tensor τ'_{ik} is represented in terms of the tensor of the coefficients of nonrelaxing viscosity a'_{ikmn} which appears in relation (22): $\tau'_{ik} = \beta a'_{ikmn} e_{mn}$ [3].

Using (18) we eliminate the thermodynamic parameter λ_{mn} from relation (19). In so doing we pass from the derivative d'/dt in the co-moving reference system to the material derivative d/dt in the laboratory reference system in accordance with the relation

$$\frac{d' A_{ik}}{dt} = \frac{dA_{ik}}{dt} - v_{i,n} A_{nk} - v_{j,n} A_{in} \tag{23}$$

for the second-rank tensor A_{ik}. With allowance for the above remarks, Eq. (19) takes the form

$$\tau_{ik} + \lambda \frac{d' \tau'_{ik}}{dt} + \tau'_{im} v_{k,m} + \tau'_{mk} v_{j,m} = -P\delta_{ik} + \beta U_{ikmn} e_{mn} + \beta A_{ikmn} \left(J_{mn} v_{l,l} + \frac{d' J_{mn}}{dt} \right), \tag{24}$$

where we have introduced the notation $U_{ikmn} = a'_{ikmn} - \beta A_{ikjl} L^{j,\tau}_{jlmn}$ and $A_{ikmn} = L^{\tau,j}_{ikps} (L^{j,j})^{-1}_{psmn}$.

We note that Eq. (24) established within the framework of nonequilibrium statistical mechanics coincides in form with the corresponding equations obtained based on the phenomenological approach [1] and it is its statistical substantiation. Unlike the phenomenological consideration, the material kinetic coefficients are determined in the form of the time correlation functions of the corresponding fluxes, which provides the basis for their evaluations and prediction from the first principles.

Let us apply the theory constructed above to consideration of the rheological properties of the liquid-crystalline polymeric system in the case of plane shear flow. We confine ourselves to steady-state processes, which enables us to use Eq. (24) in the form

$$\tau_{ik} + \tau'_{im} v_{k,m} + \tau'_{mk} v_{j,m} + v_m \tau'_{ik,m} = -P\delta_{ik} + \beta U_{ikmn} e_{mn} + \beta A_{ikmn} (J_{mn} v_l)_{,l} \,. \tag{25}$$

We will consider the liquid-crystalline polymer between two infinite surfaces the distance between which is equal to $2h$; one surface is at rest, while the other moves in parallel to the first surface with a constant velocity **V**. If we introduce the coordinate system (x_1, x_2, x_3), the x_1 axis of which is directed in parallel to **V**, the x_2 axis of which is perpendicular to the surfaces, and the x_3 axis of which is perpendicular to the first two axes, then the field of velocities will have only a single nonzero component, i.e., $\mathbf{v}(\mathbf{x}) = (v(x_2), 0, 0)$ and the components of the director which shows the direction of predominant orientation of the structural elements of the medium are determined in terms of the angle θ between the director and the direction of the hydrodynamic flow: $\mathbf{n}(\mathbf{x}) = (\cos \theta(x_2), \sin \theta(x_2), 0)$. Then the field of deformation rates will have just a single nonzero component $\gamma = v_{1,2}$.

Upon substitution into (25) we arrive at the following formulas for the components of the stress tensor in the coordinate system in question:

$$\begin{gathered}
\tau_{21}(\theta, \gamma) = A_{21}(\theta)\,\gamma + B_{21}(\theta)\,\gamma^2 , \\
\tau_{11}(\theta, \gamma) = A_{11}(\theta)\,\gamma + [B_{11}(\theta) - \lambda A_{21}(\theta)]\,\gamma^2 - \lambda B_{21}(\theta)\,\gamma^3 , \\
\tau_{22}(\theta, \gamma) = A_{22}(\theta)\,\gamma + [B_{22}(\theta) - \lambda A_{21}(\theta)]\,\gamma^2 - \lambda B_{21}(\theta)\,\gamma^3 , \\
\tau_{12}(\theta, \gamma) = A_{12}(\theta)\,\gamma + [B_{12}(\theta) - \lambda(A_{11}(\theta) + A_{22}(\theta))]\,\gamma^2 - \\
- \lambda\,[B_{21}(\theta) + B_{22}(\theta) - 2\lambda A_{21}(\theta)]\,\gamma^3 + \lambda^2 A_{21}(\theta)\,\gamma^4 ,
\end{gathered} \tag{26}$$

where the coefficients of the powered deformation rates are determined in terms of the coefficients of the material tensors appearing in Eqs. (18) and (19).

The obtained nonlinear material relations together with the equation of motion of the liquid-crystalline polymeric system (equations of momentum balance and moment of momentum) form a rather complex system of nonlinear differential equations for the functions $\theta(x_2)$ and $\gamma(x_2)$ even in such a simple case; this system can be solved using the corresponding numerical methods.

We compare the results obtained and the existing experimental data for an acetoxypropylcellulose (APC) liquid-crystalline polymeric system with a molecular weight of 94,000 and 129,000 [5, 6]. To do this it is convenient to introduce the so-called first

$$N_1 = \tau_{11} - \tau_{22} \tag{27}$$

and second

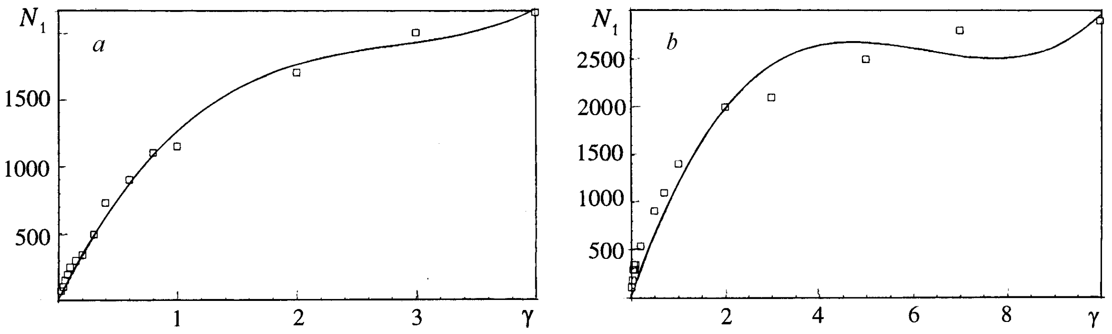

Fig. 1. First difference of stresses N_1 vs. deformation rate γ: a) for APC-94,000 and b) APC-129,000 (solid curve, theory; symbols denote: a) experiment [5] and b) [6]). N_1, Pa; γ, sec^{-1}.

$$N_2 = \tau_{22} - \tau_{33} \tag{28}$$

differences of normal stresses. Then formulas (26) will take the form

$$\begin{gathered} N_1 = \beta\lambda\gamma \left[c_{11} - c_{22} - \lambda\gamma \left(c_{12} + c_{21} \right) - 2 \left(\lambda\gamma \right)^2 c_{11} \right] , \\ N_2 = \beta\lambda\gamma \left(c_{11} - c_{33} \right) - N_1 , \\ \tau_{12} \left(\theta, \gamma \right) = \beta\lambda\gamma \left[c_{12} + \lambda\gamma c_{11} \right] , \end{gathered} \tag{29}$$

where the quantities c_{ij} are functions of the angle θ and they are determined by the coefficients of the material tensors appearing in Eqs. (18) and (19).

The results of the comparison of theoretical calculations and experimental data for the first difference of stresses are presented in Fig. 1. As is clear from the indicated plots, the theory satisfactorily describes the behavior of the first difference of stresses with variation of the rate of shear deformation of the medium.

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NOTATION

N, number of molecules in the system; n, number of atoms in the molecule; $\mathbf{v}$, velocity of hydrodynamic motion of the medium; $\hat{\tau}_{ik}(\mathbf{x})$, microscopic stress tensor; $\hat{\pi}_{ik}(\mathbf{x})$, microscopic moment-stress tensor; $\hat{J}_k^H$, $\hat{J}_{ijl}^J$, and $\hat{t}_{ikl}$, microscopic densities of the energy fluxes, the ordering parameter, and the generalized moment of momentum respectively; $\mathbf{v}(\mathbf{x}, t)$, average velocity of macroscopic motion of the medium; $\boldsymbol{\omega}(\mathbf{x}, t)$, average angular velocity of rotation of the structural elements; $\varphi_{ij}(\mathbf{x}, t)$, average rate of deformation of the structural element; $e_{nm} = \partial v_m / \partial x_n - e_{knm}\omega_k$, deformation-rate tensor; P, pressure; λ_{mn}, tensor thermodynamic parameter conjugate to the average density of the moment of inertia. Subscript: $^\wedge$, microscopic quantity.

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