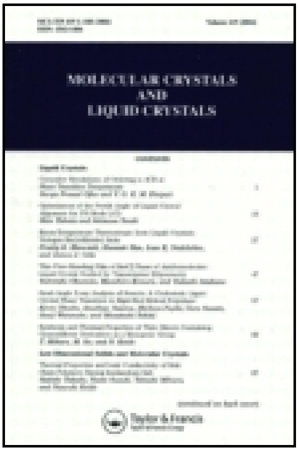

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# Statistical Theory of Hydrodynamic and Relaxation Processes in Liquid Crystals

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# STATISTICAL THEORY OF HYDRODYNAMIC AND RELAXATION PROCESSES IN LIQUID CRYSTALS

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Abstract The general methods of nonequilibrium statistical thermodynamics are used to describe viscoelastic properties of nematic liquid crystals and their approximate design formulas are derived.

A molecular-statistical approach in hydrodynamics of liquid crystals (LC) is aimed to ground the structure of the known phenomenological equations[1], to find microscopic quantities whose correlations specify macroscopic properties of LCs and to predict macroscopic characteristics from the first principles.

A list of macroscopic variables incorporates traditional ones obeying the local balance equations

$$\dot{\rho}=-\nabla_i p_i,\ \dot{p}_i=\nabla_j \tau_{ij},\ \dot{h}=-\nabla_l j_l,\ e_{ikl}\tau_{lk}+M_i=0. \tag{1}$$

Here $\rho$ , $p_i$ and $h$ are the densities of mass, momentum and energy; $\tau_{ij}$ the stress tensor; $M_i$ the volume density of moment of couple; $j_i$ the energy flow.

The balance equations are derived by nonequilibrium statistical operator method[2] averaging of microscopic analogs of these equations. In deriving the latter, the explicit expressions are found for the microscopic stress tensor $\hat{\tau}_{ij}$ and flow energy $\hat{j}_i$ [3].

The specific features of a LC phase is allowed for by a tensor orientation-order parameter. As this parameter, use is made of the quadrupolar term in the mass density [4]

$$\hat{R}_{ij}(\vec{x})=\sum_{\nu=1}^{N}\left(\sum_{\alpha=1}^{n} m_{\alpha\nu}\left(y_i^{\alpha\nu} y_j^{\alpha\nu}-3^{-1}\delta_{ij}\left(y_k^{\alpha\nu}\right)^2\right)\right)\delta(\vec{x}-\vec{x}^{\nu}). \tag{2}$$

Here $\vec{x}^{\nu}$ is the radius-vector at the centre of mass of a molecule composed of n atoms; $\vec{y}^{\alpha\nu}$ the radius-vector of an atom with a mass $m_{\alpha\nu}$ taken from the centre of mass of a molecule $\nu$; $N$ the total number of molecules in a system; $\vec{x}$ the radius-vector of a point in space, and $\delta(\vec{x}-\vec{x}^{\nu})$ the delta-function.

The equation of motion for $\hat{R}_{ij}$ is of the form

$$\dot{\hat{R}}_{ij}=2\left(\hat{L}_{ij}-3^{-1}\delta_{ij}\hat{L}_{kk}\right)+\hat{J}_{ij},$$

where $\hat{L}_{ij}=2^{-1}\left(\hat{\mathcal{P}}_{ij}+\hat{\mathcal{P}}_{ji}\right)$, $\hat{\mathcal{P}}_{ij}=\sum_{\nu=1}^{N}\left(\sum_{\alpha=1}^{n}\pi_i^{\alpha\nu} y_j^{\alpha\nu}\right)\delta(\vec{x}-\vec{x}^{\nu})$, (3) $\vec{\pi}^{\alpha\nu}$ is the momentum conjugated by $\vec{y}^{\alpha\nu}$, and $\hat{J}_{ij}$ is the source density.

A simple relation, in the form of $R_{ij}\infty(n_i n_j-3^{-1}\delta_{ij})$, between a director $n_i$ and an order parameter $R_{ij}$ valid at equilibrium and near it cannot be shifted to a nonequilibrium region. Therefore, use is made of a dynamic density of a small rotation angle $\hat{\Theta}_i(\vec{x})=\sum_{\nu=1}^{N}\Theta_i^{\nu}\times\delta(\vec{x}-\vec{x}^{\nu})$ where $\Theta_i^{\nu}$ is the small rotation angle of a molecule with a number $\nu$.

The equation of motion for $\hat{\Theta}_i$

$$\dot{\hat{\Theta}}_i(\vec{x})=\sum_{\nu=1}^{N}\omega_i^{\nu}\delta(\vec{x}-\vec{x}^{\nu})-\nabla_k\left(\sum_{\nu=1}^{N} m^{-1}p_k^{\nu}\Theta_i^{\nu}\delta(\vec{x}-\vec{x}^{\nu})\right), \tag{4}$$

reduces to the one for director evolution after nonequilibrium averaging is made. Here $\omega_i^{\nu}$ is the angular velocity of a molecule; $p_k^{\nu}$ the molecule momentum and $m$ the molecule mass.

Averaging the tensor $\hat{\tau}_{ij}$ and Eqs.(3) and (4) yields the relations of statistical hydrodynamics of LCs

$$\tau_{ij} = -\mathcal{P}\delta_{ij} + a_{ijkl}\varepsilon_{kl} + E_{klij}\nu_{kl} - \lambda_{kij}M_k ,$$
$$e_{ikl}n_k\dot{n}_l = \omega_i + \lambda_{ikl}\varepsilon_{kl} - A_{kli}\nu_{kl} + b_{ik}M_k ,$$
$$\dot{R}_{ij} = -F_{ijkl}\nu_{kl} + \beta E_{ijkl}\varepsilon_{kl} + \beta A_{ijk}M_k \qquad (5)$$

Here $\beta^{-1} = kT$ is the reverse temperature; $\varepsilon_{ij} = \nabla_j v_i - \omega_k e_{kij}$; $v_i$ the hydrodynamic velocity; $\omega_i$ the mean angular velocity of the proper rotation of a molecule; $e_{ikl}$ the Levi-Civita symbol; $M_i = e_{ijl}n_j h_l$; $h_l$ the molecular field[1]; $\mathcal{P}$ the pressure; $\nu_{ij}$ the thermodynamic parameter conjugated by $R_{ij}$. A relation exists between them: $R_{ij} = g_{ijkl}\nu_{kl}$. Here $g_{ijkl}$ is the static correlation function of $\hat{R}_{ij}$. For simplicity, the relation for an incompressible isothermal medium is written. A general case has been considered earlier[3].

The tensors $a_{ijkl}$, $b_{ik}$, $E_{ijkl}$, $\lambda_{ijl}$, $A_{ijl}$ and $F_{ijkl}$ are expressed by Green-Kubo-like formulas in the form of time integrals of time correlation functions (TCF) of the appropriate microscopic quantities[3]. A tensor structure is specified, considering the symmetry of nematics falling into a group $D_{\infty h}$.

For uniaxial LCs, the relaxation of the order parameter $R_{ij}$ is characterized by three relaxation times expressed in terms of tensor components $F_{ijkl}$ and $g_{ijkl}$.

After the internal parameters $R_{ij}$ and $\nu_{ij}$ are omitted from Eqs.(5), considering the relation $e_{ikl}\tau_{lk} + M_i = 0$, one obtains the hydrodynamics equations for nematics and the expression for viscosity coefficients in terms of the tensor components entering into Eqs. (5).

The statistical equations refer to a class of the ones of generalized relaxation hydrodynamics. These are of the form of the equations of the phenomenological theory[1] but with material characteristics as a function of frequency determined by the relaxation of the order parameters $R_{ij}$.

The TCFs determining the viscosity coefficients are calculated approximately by Fokker-Planck's equation for a rotational distribution function and equilibrium averaging in the approximation of an average field. It is characterized by the effective potential energy of a molecule

$$u = -3 \cdot 2^{-1} kTbs\cos^2\Theta ,$$

$s$ is the ordering degree and $\Theta$ is the angle between a director and a major molecule axis. The interaction intensity is taken into account by the parameter $b$.

The below formulas relate the viscosity coefficients to the number particle density $n$, to the rotational friction coefficient $\zeta$, to the quantity $s$, and to the parameter $\chi$ characterizing the shape of a molecule. As an example, let us present the expressions[5] for some viscosity coefficients in the notations of the publication[1]

$$\gamma_1 = 3\zeta n s^2(1+6^{-1}bq)/[q+(2+s)s^2(1+6^{-1}bq)+6s^2-1{,}5bs^4],$$

$$\alpha_4 = 2\cdot 3^{-1}\zeta n[2r-s+3^{-1}\chi d b^{-1}]^2/(1-s+b^{-1}),$$

$$q = 2+s-4b^{-1}. \tag{6}$$

The parameters $\chi$, $r$ and $d$ are calculated by the formulas

$$\chi = \left[\left(\frac{\sigma_\parallel}{\sigma_\perp}\right)^2-1\right]\Big/\left[\left(\frac{\sigma_\parallel}{\sigma_\perp}\right)^2+1\right], \quad r=(3-\chi)/4\chi,$$

$$d = 1+3^{-1}\chi^2+2\cdot 3^{-1}\chi^2 s^2, \tag{7}$$

where $\sigma_{\parallel}$ and $\sigma_{\perp}$ are the lengths of the major and minor axes of a rotation ellipsoid modelling the shape of a molecule.

The rotational friction coefficient $\zeta$ is expressed in terms of the component of the rotational diffusion tensor normal to $\vec{n}$, i.e. $\zeta = kT/D_{\perp}$. Here the tensor $D_{ij}$ is determined by TCF of an angular molecule velocity $D_{ij} = \int_0^{\infty} dt \langle \omega_i(0) \times \omega_j(t) \rangle$ which is calculated by the Enskog method[6] generalized to liquid crystals. And, finally, $\zeta$ is expressed by the formula

$$\zeta = I\sigma_{\perp}^{2} n\sqrt{\pi/\beta m}\, \exp(-\beta\varepsilon)\left[2/9 + (21\chi - 10\chi s/3)/105\right], \tag{8}$$

where $I$ is the moment of inertia of a molecule relative to its " minor " axis and $\varepsilon$ is the potential of mean force of a pair of molecules at contact included into the binary distribution function $g = \exp(-\beta\varepsilon)$ .

Calculation by the above formulas satisfactorily agrees with the experimental data on the viscosity coefficients for a number of nematics. The advantage of the theory is that the viscosity coefficients as a function of molecular parameters may be allowed for in an explicit form.

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