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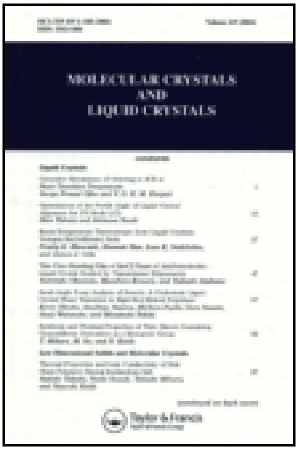

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The Molecular Theory for the Viscosity of Nematic and Smectic C Liquid Crystals

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The Molecular Theory for the Viscosity of Nematic and Smectic C Liquid Crystals

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The rotational diffusion of a rod-like molecule in nematic and smectic C liquid crystals, and also in two-component nematic mixtures, is considered in the molecular-field approximation. The microscopic friction constant, which determines the molecular rotation drag, possesses an exponential temperature dependence with the activation energy determined by the isotropic part of the intermolecular interaction energy. The nematic Leslie coefficients are obtained in terms of molecular parameters. Their values, signs and the temperature variation qualitatively correspond to experimental data. An additional activation energy, proportional to the nematic order parameter, appears in the expressions for the rotational viscosity coefficients γ_1 and $\gamma_\perp$ both in nematics and C smectics. All Leslie coefficients possess complicated behavior with varying mixture concentration. In particular, the rotational viscosity coefficient γ_1 is proportional to a third-order polynomial in concentrations ρ_A and ρ_B with coefficients $\propto \sqrt{J_A\rho_A + J_B\rho_B}\exp(J_A\rho_A + J_B\rho_B)$.

Keywords: viscosity, molecular theory, nematic-smectic C

The energy dissipation in a flowing uniaxial nematic liquid crystal is determined by the viscous stress tensor $\sigma_{\alpha\beta}$, which takes the form in the case of a non-compressible liquid[1]:

$$\sigma_{\alpha\beta} = a_1 n_\alpha n_\beta n_\mu n_\rho A_{\mu\rho} + a_4 A_{\alpha\beta} + a_5 n_\alpha n_\mu A_{\mu\beta} + a_6 n_\beta n_\mu A_{\mu\alpha} + a_2 n_\alpha N_\beta + a_3 n_\beta N_\alpha \tag{1}$$

where $A_{\alpha\beta} = 1/2(\partial_\alpha v_\beta + \partial_\beta v_\alpha)$-the symmetrical part of the flow velocity gradients tensor $g^{\alpha\beta}$; $N_\alpha = \dot{n}_\alpha - [\vec{\omega} \times \vec{n}]_\alpha$, where $\vec{\omega} = 1/2 \text{ Rot } \vec{v}$. Here the unit vector $\vec{n}$ is the nematic director, $\vec{\omega}$-the flow rotation angular velocity. The viscosity constants α_1–α_6 in Equation (1) are the so called Leslie coefficients, which satisfy the general Parodi relation $a_2 + a_3 = a_6 - a_5$. The rotational viscosity coefficient $\gamma_1 = a_3 - a_2$ corresponds to the pure director rotation $\dot{\vec{n}}$. It is a very important parameter of

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LC materials because it determines the reorientation times of various applied systems. γ_1 (like the other Leslie coefficients) strongly depends on the temperature and is very sensitive to a molecular structure.

A more or less consistent approach to the description of rheological properties of nematic liquid crystals has been proposed by Kuzuu and Doi[2] and Hess[3] using the model of suspension. Within the framework of one-particle suspension model Kuzuu and Doi succeeded in obtaining the exact expression for the symmetrical part of the macroscopic stress tensor. On the other hand, the evaluation of the pure rotational effects required the explicit expression for the one-particle distribution function, which was not obtained in Reference (2). It should be noted also, that the Leslie coefficients, presented by Kuzuu and Doi, do not possess any exponential temperature dependence which is usually observed in experiments.

In our works[4,5] we make an attempt to solve some problems which remained obscure in previous approaches and present the explicit expressions for the rotational viscosity coefficients of a nematic. Also we'll try to consider more complicated systems, namely, smectic C liquid crystals, where the rotational viscosity coefficient $\gamma_\perp$ (describing the pure director rotation about the layer normal axis) is a very important parameter for applications of ferroelectric smectics, and also-the two component nematic mixture.

In the general case one should account for molecular biaxiality and (probably) the polar interaction in the smectic C case. But, considering the local order, these contributions are small in the total intermolecular potential, and form small corrections to the viscous coefficients. Neglecting these contributions in a first approximation one can develop a theory very similar to that in the nematic case, accounting for certain geometrical restrictions in the smectic C phase.

Usually mixtures of different compounds are used as nematic materials and the problem of choosing the proper substances and the mixture concentration arises in order to obtain the desired macroscopic characteristics. That is why it is important to extend our microscopic theory to the case of different sorts of molecules, interacting in the media, and to make it possible to predict the values of the viscosity coefficients of a mixture, if the concentration and the molecular characteristics are defined.

The microscopic stress tensor of a condensed matter describes the evolution of a microscopic momentum density $\vec{p}(\vec{r})$, according to the local conservation law

$$\frac{\partial}{\partial t}\vec{p}(\vec{r}) = -\mathrm{Grad}\,\hat{\sigma}^M(\vec{r}) \tag{2}$$

In order to obtain the expression for the momentum density one should use some model description. Let us suppose here that our system consists of uniaxial rod-like molecules of the length L and breadth D and consider a molecule as a rigid aggregate of bounded points of a mass m_k. In this case

$$\vec{p}(\vec{r}) = \sum_i \sum_k m_k(\vec{v}_i + [\vec{\omega}_i \times \vec{r}_{ik}])\,\delta\,(\vec{r} - \vec{r}_i - \vec{r}_{ik}) \tag{3}$$

where the index "i" describes the summation over the molecules and "k"-over the

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points inside each molecule; $\vec{\omega}_i$ - is the angular velocity of molecular rotation, $\vec{v}_i$ - the velocity of its center of mass. The $\vec{r}_i$ vector denotes the position of the center of mass and $\vec{r}_{ik}$ is the position of the point "k" in the molecular frame so that the velocity $\vec{v}_{ik} = \vec{v}_i + [\vec{\omega}_i \times \vec{r}_{ik}]$ in Equation (3) is the velocity of a point "k" of the "i"-th molecule in the laboratory frame.

In the simplest case of a pure nematic liquid crystal one can obtain the orientational part of the stress tensor $\hat{\sigma}^M(\vec{r})$, which takes the form (see Reference (4)):

$$\sigma^{\text{or.}}_{\alpha\beta} = -\sum_i [I_i^{\gamma\alpha}(I_i^{-1})^{\nu\mu}\Gamma_i^{\mu}\varepsilon_{\beta\nu\gamma} + I_i^{\delta\rho}\varepsilon_{\alpha\gamma\delta}\omega_\gamma\varepsilon_{\beta\mu\rho}\omega_\mu$$

$$+ I_i^{\mu\alpha}\omega_\beta\omega_\mu - I_i^{\alpha\beta}\omega^2]\delta(\vec{r} - \vec{r}_i), \quad (4)$$

where $I_i^{\alpha\beta} = \Sigma\, m_k r^{\alpha}_{ik} r^{\beta}_{ik}$ is the inertia tensor and $\vec{\Gamma}_i$ is the total moment of force, acting on the "i"-th molecule. Introducing the unit vector $\vec{a}$ in the long molecular axis direction, one can write down:

$$I^{\alpha\beta} = I_\perp\delta_{\alpha\beta} + (I_\parallel - I_\perp)a_\alpha a_\beta,$$

$$\Gamma^\alpha(\vec{r}_i) = -\sum_j \varepsilon_{\alpha\beta\gamma}a^i_\beta \frac{\partial}{\partial a^i_\gamma} U(\vec{a}^i, \vec{a}^j, \vec{r}_{ij}) \quad (5)$$

where $U(\vec{a}^i, \vec{a}^j, \vec{r}_{ij})$ is the intermolecular interaction potential for molecules "i" and "j". We use the model Reference (6) for this potential, which accounts for the isotropic and anisotropic attraction forces; the steric repulsion forces will be accounted for by the corresponding step-function during statistical integration over configurations.

$$U(1, 2) \simeq -G\frac{D^6}{r^6_{12}} - \frac{D^6}{r^6_{12}}[I_0(\vec{a}_1 \cdot \vec{a}_2)^2 + I_2(\vec{a}_1 \cdot \vec{a}_2)(\vec{a}_1 \cdot \vec{\mu}_{12})(\vec{a}_2 \cdot \vec{\mu}_{12})] \quad (6)$$

where $\vec{\mu}_{12} = \vec{r}_{12}/|\vec{r}_{12}|$ and coupling constants G, I_0, I_2 have the dimensionality of energy. A more detailed form of the pair interaction potential, containing higher order orientational harmonics, is not essential for the qualitative results, presented in this paper.

It can be easily shown, that in the case of a mixture of different sorts of molecules the microscopic molecular stress tensor $\hat{\sigma}^M$, which is determined by the same local conservation law (Equation (2)), transforms to the sum of contributions from each component. The form of pair potential also remains the same as in the Equation (6); one should take into account the different values of coupling constants, when different sorts of molecules with different parameters are involved in this interaction: G^{AA}, G^{BB} and G^{AB} for isotropic, and I^{AA}, I^{BB} and I^{AB} for anisotropic parts of $U(1, 2)$. In order to derive the continual hydrodynamics, one has to obtain the nonequilibrium correction to the distribution function of the molecular coordinates $w_1 = w_0(\vec{a}, \vec{n})(1 + h_{\mu\rho}(\vec{a}, \vec{n})g^{\mu\rho})$, where w_0 is the locally equilibrium function and

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the stationary correction is proportional to the small gradients of the flow velocity: $g^{\mu\rho} = \partial v_\mu / \partial x_\rho$. Then Equation (1) is the average of Equation (4) with this correction.

In the case of a smectic C liquid crystal we'll consider the simplest configuration: undistorted layers and a constant tilt angle Θ (this situation is usual for the SSFLC-surface stabilized ferroelectric liquid crystal, Reference (7)). Let us introduce unit vectors $\vec{d}$-along the layer normal and $\vec{c}$-along the projection of the long molecular axis $\vec{a}$ on the layer plane: $\vec{a} = \vec{d} \cos \Theta + \vec{c} \sin \Theta$, and the coordinate frame associated with $\vec{a}$ and the director $\vec{n}$ projection $\vec{n}\text{-}(\vec{n} \cdot \vec{d})\vec{d}$ so that the molecule equilibrium position corresponds to zero angle φ in the layer plane. In the system under consideration the vector $\vec{c}(\varphi)$ is the only relevant microscopic variable. One can obtain the semctic C microscopic stress tensor. In the mean field approximation (after the averaging over the angular velocity, see Reference (5)) we have:

$$\sigma_{\alpha\beta} \simeq \rho(I_\parallel - I_\perp) \frac{kT}{I_\perp} \left([\vec{c} \times \vec{d}]_\alpha [\vec{c} \times \vec{d}]_\beta - \frac{1}{2} (c_\alpha d_\beta + c_\beta d_\alpha) \cos \Theta \sin \Theta \right.$$

$$\left. - c_\alpha c_\beta \sin^2\Theta \right) + \rho[\varepsilon_{\alpha\beta\nu}(d_\nu - c_\nu ctg\Theta) + (c_\alpha + d_\alpha ctg\Theta)[\vec{c} \times \vec{d}]_\beta] \frac{\partial U}{\partial \varphi} \quad (7)$$

The smectic C rotational viscous coefficient $\gamma_\perp$ is usually determined by the expression for the entropy production, which takes the form at the constant tilt angle Θ Reference (1):

$$T\dot{S} = \int \gamma_\perp \sin^2\Theta \dot{\Phi}^2 d\vec{r}, \qquad \text{where } n_{\perp x} = \cos\Phi,\ n_{\perp y} = \sin \Phi.$$

Therefore, one has to determine the nonequilibrium smectic C orientational distribution function in the form $w_1 = w_0(\varphi)\,(1 + h(\varphi)\dot{\Phi})$, where the correction is proportional to the angular velocity of the C-director rotation $\dot{\Phi}$. Then, by averaging the corresponding microscopic expression one can derive the $\gamma_\perp$ viscous coefficient.

Determination of the nonequilibrium distribution functions for the molecular orientation in all systems under consideration is the main achievement of our theory; the detailed description of the Fokker-Planck equation derivation and solution can be found in our previous works.[4,5] Let us present here only the results of these works for the Leslie coefficients of the pure nematic liquid crystal, the rotational viscous coefficient of the smectic C and of the nematic mixture.

$\alpha_1 \div \alpha_6$ can be written in the following form using only definite molecular parameters:

$$\alpha_1 = -\rho\lambda \frac{p^2 - 1}{p^2 + 1} \langle P_4 \rangle, \qquad \alpha_4 = \frac{\rho\lambda}{35} (7 - 5 \langle P_2 \rangle - 2 \langle P_4 \rangle),$$

$$\alpha_2 = -\frac{\rho\lambda}{2} \langle P_2 \rangle - \frac{1}{2} \gamma_1 \simeq -\frac{\rho\lambda}{2} \left[\langle P_2 \rangle + \frac{1}{6} \sqrt{J/kT}\, e^{J/kT} \right],$$

$$\alpha_3 = -\frac{\rho\lambda}{2} \langle P_2 \rangle + \frac{1}{2} \gamma_1 \simeq -\frac{\rho\lambda}{2} \left[\langle P_2 \rangle - \frac{1}{6} \sqrt{J/kT}\, e^{J/kT} \right],$$

$$\alpha_5 = \frac{\rho\lambda}{2}\left[\frac{p-1}{p^2+1}\left(\frac{3}{7}\langle P_2\rangle + \frac{4}{7}\langle P_4\rangle\right) + \langle P_2\rangle\right],$$

$$\alpha_6 = \frac{\rho\lambda}{2}\left[\frac{p^2-1}{p^2+1}\left(\frac{3}{7}\langle P_2\rangle + \frac{4}{7}\langle P_4\rangle\right) - \langle P_2\rangle\right], \tag{8}$$

where $\rho = N/V$ is the number density, $p = L/D$ is the molecular length-to-breadth ratio, $\langle P_2\rangle$ and $\langle P_4\rangle$ are averages of corresponding Legendre polynomials with respect to the scalar product $(\vec{a} \cdot \vec{n})$; these averages are equal to the regular and second-order nematic order parameters. The mean field coupling constant, which appears in Equations (8), can be obtained by the averaging of pair potential $U(1, 2)$ over all possible positions and orientations of the second particle; the result is: $J \simeq 2\pi\rho D^3\ (9L/8D\ G + I_2 + 2/3\ I_0)\ \langle P_2\rangle$. The microscopic friction constant is estimated to be

$$\lambda \simeq 100\rho^2 D^6 \left(\frac{D}{L}\right)^2 \frac{(kT)^5}{(G)^3} \sqrt{I_\perp/kT}\, \exp\left(3\,\frac{G + I_0}{kT}\right)$$

The smectic C rotational viscosity, besides the Arrhenius law similar to that of the nematic constant γ_1 in Equation (8), possesses a remarkable dependence on the tilt angle Θ:

$$\gamma_\perp \simeq 120\sqrt{\frac{2\Delta + 1}{\Delta + 1}}\,\frac{\rho\lambda^2}{\sqrt{I_\perp J}}\exp\left(4\,\frac{\Delta + 1}{2\Delta + 1}\,\frac{J\sin^4\Theta}{kT}\right). \tag{9}$$

where $\Delta = I_\perp/I_\parallel >> 1$, parameters J and λ are the same as in Equation (8).

In the case of a nematic mixture (components of which are denoted by letters A and B) the nematic rotational viscous coefficient takes the form:

$$\gamma_1 \simeq \frac{1}{6}\left\{\rho_A\lambda^A\sqrt{\frac{J^A}{kT}}\,e^{J^A/kT} + \rho_B\lambda^B\sqrt{\frac{J^B}{kT}}\,e^{J^B/kT}\right\}, \tag{10}$$

where the friction constants for each mixture component are:

$$\lambda^A \approx 100D^6\left(\frac{D}{L_A}\right)(kT)^5\sqrt{I_\perp^A/kT}\left\{\rho_A^2\left(\frac{1}{G^{AA}}\right)^3 e^{3GAA/kT}\right.$$

$$\left. + \rho_A\rho_B\left(\frac{3}{(G^{AB} + 2G^{AA})G^{AB}}\right)^{3/2} e^{(GAA + 2GAB)/kT}\right.$$

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$$+ \rho_B^2 \left(\frac{3}{2G^{AB} + G^{BB}}\right)^3 e^{(2G^{AB} + G^{BB})/kT} \Bigg\}$$

and the similar expression for λ^B, where $D \approx (D_A + D_B)/2$, and $J^{A,B}$ are the coupling constants of the mean field potential, which affects the given sort of molecules:

$$J^A \approx 2\pi\rho_A \left(\frac{9L_A}{8D_A} G^{AA} + I_2^{AA} + \frac{2}{3} I_0^{AA}\right) D_A^3 + 2\pi\rho_B \left(\frac{9L_A}{8D} G^{AB} + I_2^{AB} + \frac{2}{3} I_0^{AB}\right) \left(\frac{D_A + D_B}{2}\right)^3,$$

(and a similar expression for J^B).

In conclusion of this very short article let us note, that, unfortunately, we were not able to present the statistical part of our theory here–the details one can find in the papers[4,5] devoted to the different branches of this theory. It should be noted also, that the results of the present theory are not limited by the determination of viscous coefficientes. Indeed, the kinetic equation for the one-particle distribution function of the rotating system and its stationary solution can be used in the calculations of other kinetic coefficients. The non-stationary solution of this equation can yield different relaxation times which are necessary for the description of various spectroscopic experiments. For example, the average time of the molecular long axis reorientation in pure nematics is: $\tau_\perp \approx \pi\lambda(kT/J)^{3/2}\exp[J/kT]/4kT$; the estimation of the time of azimuthal relaxation in smectic C phase is:

$$\tau_\varphi \approx \frac{\pi}{\frac{\Delta + 1}{2\Delta + 1}\sin^4\Theta} \frac{\lambda}{J} \exp\left(4\frac{\Delta + 1}{2\Delta + 1}\frac{J\sin^4\Theta}{kT}\right)$$

Many predictions could be made on the basis of our results for the nematic mixture (Equation (10)) since it represents together with the concentration dependence, the influence of different molecular parameters on the macroscopic viscosity coefficients.

Some results of the present theory, namely the microscopic expressions for viscous coefficients in pure nematic liquid crystal, have been recently verified in details and compared with other existing theoretical models.[8] It was shown, that an agreement of our predictions with different measurements in a wide class of materials is quite good. This proves that the model and approximations, used in our works are acceptable for microscopic description of transport processes in nematic liquid crystals and that the other results, concerning smectics C and nematic mixtures, can adequately describe these systems as well.

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