Rotational Diffusion and Rheological Properties of Liquid Crystals

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Z. Naturforsch. **44a,** 785–792 (1989); received November 23, 1988

The rotational diffusion of a rod-like molecule in a liquid crystal is considered in the molecular-field approximation, and the corresponding Fokker-Planck equation is derived. It is shown that the microscopic friction coefficient, which is the parameter of this equation, possesses the usual exponential temperature dependence with the activation energy determined by the isotropic part of the intermolecular interaction energy. The viscous stress tensor of the nematic is obtained by averaging of the corresponding microscopic expression with the non-equilibrium distribution function. Finally, explicit expressions for the Leslie coefficients are obtained in terms of molecular parameters. Their values, signs and temperature variation correspond qualitatively to experimental data.

1. Introduction

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

$$\sigma_{\alpha\beta} = \alpha_1 n_\alpha n_\beta n_\mu n_\varrho A_{\mu\varrho} + \alpha_4 A_{\alpha\beta} + \alpha_5 n_\alpha n_\mu A_{\mu\beta} + \alpha_6 n_\beta n_\mu A_{\mu\alpha} + \alpha_2 n_\alpha N_\beta + \alpha_3 n_\beta N_\alpha , \qquad (1)$$

where $A_{\alpha\beta} = \frac{1}{2}(\partial_\alpha v_\beta + \partial_\beta v_\alpha)$ is the symmetrical part of the flow velocity gradients tensor $g^{\alpha\beta}$ and $N_\alpha = \dot{n}_\alpha - [\boldsymbol{\omega} \times \boldsymbol{n}]_\alpha$ with $\boldsymbol{\omega} = 1/2 \operatorname{rot} \boldsymbol{v}$. Here the unit vector $\boldsymbol{n}$ is the nematic director and $\boldsymbol{\omega}$ the flow rotation angular velocity. The viscous coefficients $\alpha_1 - \alpha_6$ in (1) are the so called Leslie coefficients, which satisfy the general Parodi relation $\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5$. The complicated form of the stress tensor (1) is caused by the nematic anisotropy and corresponds to the various interactions between flow and director orientation. In the isotropic phase all Leslie coefficients, except α_4, vanish, while α_4 becomes the isotropic shear viscosity coefficient.

The viscosity coefficients are very important parameters of LC materials (see [2]). They strongly depend on the temperature and are very sensitive to the molecular structure [3]. That is why it is interesting to develop a molecular theory of the rheological properties of nematics which could account for the dependence of the Leslie coefficients on the molecular parameters, temperature, order parameter and so on. Such expressions have for the first time been obtained by Diogo and Martins [4–6]. It should be noted, however, that the results of [4–6] are not based on any consistent statistical theory but are obtained from qualitative, semi-empirical relations. By analogy with viscosity investigations of other molecular systems, Diogo and Martins supposed that the Leslie coefficients are proportional to the characteristic nematic relaxation time, which is related to the probability of overcoming the potential barrier during the molecular reorientation. This barrier is determined by the average molecular field acting on the molecule, and also by the free volume needed for the molecular reorientation [5]. In this way the exponential temperature dependence (the Arrhenius law) of the viscosity coefficients appears in the Diogo and Martins theory. This kind of temperature dependence has been observed by many authors (see, for example, [2, 7, 8]). However, there are two main contradictions between the results of Diogo and Martins and the experiments. Firstly, in the Diogo and Martins theory the activation energy is determined by the mean field potential barrier, which is proportional to the nematic order parameter, while the experimental data indicate that this energy is approximately constant throughout the nematic phase [2, 8, 9]. Secondly, there is a large difference between the experimental and calculated activation energies. Indeed, the activation energy E_{act} equals $J_0 S$ in the Diogo and Martins theory, where the coupling constant J_0 can be estimated with the Maier-Saupe theory

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to equal $4.5\,kT_c$. On the other hand, the experimental values are much higher, $E_{\mathrm{act}} \cong 0.5$ eV. It should be noted also that the theory appears to be incomplete since there is no systematic way to determine relative values and signs of different Leslie coefficients; they can be described only using many free parameters [6].

A more consistent description of the rheological properties of liquid crystals has been given by Kuzuu and Doi [10] and Hess [11] using the model of suspension. Within the framework of a one-particle suspension model Kuzuu and Doi obtained an exact expression for the symmetrical part of the macroscopic stress tensor. On the other hand, the evaluation of the antisymmetrical part required the explicit expression for the one-particle distribution function, which was not obtained in [10]. As a result, the expressions for the coefficients α_2 and α_3, presented in [10], contain a contribution which is not expressed in terms of molecular model parameters. This contribution, however, appears to be very important since it completely determines the rotational viscosity of nematics. There is another model parameter in the Kuzuu and Doi theory, which is the microscopic friction coefficient. This coefficient can also be temperature dependent, and its variation should be taken into account in final expressions.

It should be noted also that the Leslie coefficients presented by Kuzuu and Doi do not possess the exponential temperature dependence usually observed.

In the present paper we make an attempt to solve some problems which remained obscure in previous approaches and present explicit expressions for Leslie coefficients which generalized the results of Kuzuu and Doi and establish an agreement between theory and experiment.

In Sect. 2 the general expression for the microscopic stress tensor of the nematic is presented in terms of molecular moments of inertia and the intermolecular interaction potential. In Sect. 3 we derive the Fokker-Planck equation from the corresponding Langevin equations which describes the stochastic motion of a single particle. In this section an approximate expression for the microscopic friction coefficient is also obtained, and it is shown that the coefficient possesses the exponential temperature dependence with a large activation energy determined by the isotropic part of the interaction potential. We suppose that this temperature dependence determines the strong temperature variation of the Leslie coefficients. Finally, in Sect. 4 the explicit expressions for all Leslie coefficients are presented, including the expression for the rotational viscosity γ_1, which appears to possess an additional exponential temperature dependence related to the overcoming of the mean field potential barrier during molecular reorientation.

2. The Microscopic Stress Tensor

The microscopic stress tensor of condensed matter decribes the evolution of the microscopic momentum density $\boldsymbol{p}(\boldsymbol{R})$ according to the local conservation law

$$\frac{\partial}{\partial t}\, \boldsymbol{p}(\boldsymbol{R}) = -\operatorname{Grad} \hat{\sigma}^M(\boldsymbol{R})\,. \tag{2}$$

In order to obtain an expression for the momentum density one has to use some model description. In the case of nematic liquid crystals let us suppose that our system consists of uniaxial rod-like molecules and consider a molecule as a rigid aggregate of bounded points of mass m_k. In this case

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

where the index i indicates a molecule and k a point inside the molecule. $\boldsymbol{\omega}_i$ is the angular velocity of molecular rotation and $\boldsymbol{v}_i$ the velocity of its center of mass. $\boldsymbol{r}_i$ denotes the position of the center of mass and $\boldsymbol{r}_{ik}$ is the position of the point k in the molecular frame so that the velocity $\boldsymbol{v}_{ik} = \boldsymbol{v}_i + [\boldsymbol{\omega}_i \times \boldsymbol{r}_{ik}]$ in (3) is the velocity of a point k of the i-th molecule in the laboratory frame.

Taking the time derivative in (3), using the evident relations $\dot{\boldsymbol{r}}_i = \boldsymbol{v}_i$, $\dot{\boldsymbol{r}}_{ik} = [\boldsymbol{\omega}_i \times \boldsymbol{r}_{ik}]$ and formally expanding the delta-function in powers of $\boldsymbol{r}_{ik}$ ($\delta(\boldsymbol{R} - \boldsymbol{r}_i - \boldsymbol{r}_{ik}) = \delta(\boldsymbol{R} - \boldsymbol{r}_i) + (\boldsymbol{r}_{ik} \cdot \operatorname{Grad})\, \delta(\boldsymbol{R} - \boldsymbol{r}_i) + \ldots$)* one can obtain the conservation law in the form of (2). Then the orientational part of the stress tensor $\hat{\sigma}^M(\boldsymbol{R})$, which we are interested in, takes the form

$$\begin{aligned} \sigma^{\mathrm{or.}}_{\alpha\beta} = -\sum_i \big[& I_i^{\gamma\alpha} (I_{\mathrm{i}}^{-1})^{\nu\mu}\, \Gamma_i^{\ \mu}\, \varepsilon_{\beta\nu\gamma} + I_i^{\delta\varrho}\, \varepsilon_{\alpha\gamma\delta}\, \omega_\gamma\, \varepsilon_{\beta\mu\varrho}\, \omega_\mu \\ & + I_i^{\mu\alpha}\, \omega_\beta\, \omega_\mu - I_i^{\alpha\beta}\, \omega^2 \big]\, \delta(\boldsymbol{R} - \boldsymbol{r}_i)\,, \end{aligned} \tag{4}$$

where $I_i^{\alpha\beta} = \sum m_k\, r_{ik}^{\alpha}\, r_{ik}^{\beta}$ is the inertia tensor and $\boldsymbol{\Gamma}_i$ is the total moment of the force acting on the i-th molecule. Introducing the unit vector $\boldsymbol{a}$ in the direction of the

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* This expansion is justified because we are not interested in the microscopic stress itself but in its average value which should be obtained by integration with a smooth distribution function.

long molecular axis one can write

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

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

where $U(\boldsymbol{a}^i, \boldsymbol{a}^j, \boldsymbol{r}_{ij})$ is the intermolecular interaction potential for molecules i und j.

The phenomenological stress tensor is the result of statistical averaging of (4), which implies the integration over the angles ($\boldsymbol{a}$) and angular velocity ($\boldsymbol{\omega}$) with the proper distribution function. The averaging over velocity can be easily carried out since it is determined by the one-particle local Maxwell distribution function $\cong \exp[-I_{\perp}(\boldsymbol{\omega} - \boldsymbol{\Omega}(\boldsymbol{a}, \boldsymbol{r}))^2/2kT]$. The first term in (4) does not depend on $\boldsymbol{\omega}$; integrating the second term we obtain the "kinetic" part of the stress tensor $\sigma^M_{\alpha\beta}$: $-\sum\limits_i (3 I^{\alpha\beta}_i kT/I_{\perp})\,\delta(\boldsymbol{R} - \boldsymbol{r}_i)$.

In this paper we consider a nematic liquid crystal formed by rod-like molecules which are characterized by a large difference between the longitudinal and transverse inertia moments, $I_{\parallel} \ll I_{\perp}$. Using this approximation one can simplify the microscopic stress tensor expression:

$$\sigma^M_{\alpha\beta} \cong \sum_i \Bigg[3kT(a^i_{\alpha} a^i_{\beta} - \tfrac{1}{3}\,\delta_{\alpha\beta}) + \sum_{j \neq i} a^i_{\alpha}\,\frac{\partial}{\partial a^i_{\beta}}\,U(\boldsymbol{a}^i, \boldsymbol{a}^j, \boldsymbol{r}_{ij}) \Bigg]\,\delta(\boldsymbol{R} - \boldsymbol{r}_i). \tag{6}$$

In the simplest case, the averaging of (6) can be performed in the molecular field approximation, where the statistical properties of the system are determined by a one-particle distribution function. The distribution function of a nonuniformly flowing nematic can be written in the form

$$w_1 = w_0(\boldsymbol{a} \cdot \boldsymbol{n})(1 + h_{\mu\varrho}(\boldsymbol{a} \cdot \boldsymbol{n})\,g^{\mu\varrho}),$$

where w_0 is the local equilibrium function and the stationary correction is proportional to the small gradients of the flow velocity: $g^{\mu\varrho} = \partial v_{\mu}/\partial x_{\varrho}$. Then the phenomenological stress tensor in the molecular field approximation takes the form

$$\sigma_{\alpha\beta} = c \int w_0(\boldsymbol{a} \cdot \boldsymbol{n})\,h_{\mu\varrho}(\boldsymbol{a} \cdot \boldsymbol{n}) \cdot g^{\mu\varrho} \Bigg[3kT(a_{\alpha} a_{\beta} - \delta_{\alpha\beta}/3) + a_{\alpha}\,\frac{\partial}{\partial a_{\beta}}\,U(\boldsymbol{a} \cdot \boldsymbol{n}) \Bigg]\,\mathrm{d}\boldsymbol{a}, \tag{7}$$

where c is the number density and $U(\boldsymbol{a} \cdot \boldsymbol{n})$ is the orientational mean-field potential (see also [10]). Thus the macroscopic stress tensor is a functional of the stationary correction function $h_{\mu\varrho}(\boldsymbol{a} \cdot \boldsymbol{n})$, which can be obtained as the stationary solution of a proper kinetic equation.

3. Kinetic Equation

It is reasonable to consider the microscopic molecular motion in a liquid crystal as a rotational Brownian motion which should be described by the appropriate Fokker-Planck equation [11].

Let us describe briefly the main ideas of the Fokker-Planck equation derivation. The mean-field approximation means that we can consider a molecule as a particle (with the inertia tensor $I_{\alpha\beta} = I_{\perp}\,\delta_{\alpha\beta} + (I_{\parallel} - I_{\perp})\,a_{\alpha}\,a_{\beta}$) which performs rotational Brownian motion in the mean-field potential $U(\boldsymbol{a} \cdot \boldsymbol{n})$. Note that the microscopic friction arises when the instant molecular angular velocity $\boldsymbol{\Psi} = \dot{\phi}\,\boldsymbol{a} + [\boldsymbol{a} \times \dot{\boldsymbol{a}}]$ deviates from the average velocity

$$\boldsymbol{\Psi}_0 = \mathrm{Rot}\,\boldsymbol{v} + [\boldsymbol{a} \times \hat{g}_s \cdot \boldsymbol{a}](p^2 - 1)/(p^2 + 1) \quad \text{(see [12, 13])},$$

where p is the molecules length-to-breadth ratio: $p = L/d$. So the external moment of force acting on the molecule (besides the Brownian one) takes the form

$$\boldsymbol{\Gamma} = \boldsymbol{\Gamma}_{\mathrm{el.}} - \hat{\lambda} \cdot (\boldsymbol{\Psi} - \boldsymbol{\Psi}_0), \tag{8}$$

where

$$\Gamma^{\alpha}_{\mathrm{el.}} = -\varepsilon_{\alpha\beta\gamma}\,\alpha_{\beta}\,\frac{\partial}{\partial \alpha_{\gamma}}\,U\,.$$

In an uniaxial system the tensor of microscopic friction coefficients takes the form $\lambda_{kl} = \lambda(\delta_{kl} + \varepsilon_1\,a_k\,a_l + \varepsilon_2\,n_k\,n_l)$. Taking (8) into accout, one can write down the Fokker-Planck equation for the one-particle distribution function W in a phase space ($\boldsymbol{a}, \boldsymbol{\omega} = [\boldsymbol{a} \times \dot{\boldsymbol{a}}]$):

$$\frac{\partial W}{\partial t} + \varepsilon_{klm}\,a_l\,\frac{\partial}{\partial a_m}(\omega_k W) + \frac{1}{I_{\perp}}\,\frac{\partial}{\partial \omega_k}(\Gamma^k_{\mathrm{el.}}\,W) = \frac{1}{I_{\perp}}\,\lambda_{kl}\,\frac{\partial}{\partial \omega_k}\left(\omega_l - \Omega_l + \frac{kT}{I_{\perp}}\,\frac{\partial}{\partial \omega_l}\right) W, \tag{9}$$

where the average velocity of transversal rotation $\boldsymbol{\Omega}$ takes the form

$$\boldsymbol{\Omega} = \mathrm{Rot}\,\boldsymbol{v} - (\boldsymbol{a} \cdot \mathrm{Rot}\,\boldsymbol{v})\,\boldsymbol{a} + \frac{p^2 - 1}{p^2 + 1}\,[\boldsymbol{a} \times \hat{g}_s \cdot \boldsymbol{a}]$$

and the fast relaxation of the rotation about the long molecular axis $\boldsymbol{a}$ is already integrated out.

In (9) not all terms are of the same order. This fact reflects the two-step relaxation of the disribution function W (see, for example, [14]). Indeed, the statistical system rapidly relaxes to the Maxwell-like velocity distribution $W \propto \exp[-I_\perp(\boldsymbol{\omega}-\boldsymbol{\Omega})^2/2kT]$ with the corresponding relaxation time $\tau_\omega \propto I_\perp/\lambda$. Then, keeping this local equilibrium, it slowly relaxes to the Boltzmann distribution over the angular coordinates. The relaxation time ratio $\tau_\omega/\tau_a=\sqrt{I_\perp kT}/\lambda$ is a small parameter in (9). So, averaging the dimensionless equation (9) over the velocity $\boldsymbol{\omega}$ and keeping the leading terms over the parameter $\varepsilon=\sqrt{I_\perp kT}/\lambda \ll 1$, one obtains the distribution function in the form

$$W=\exp\{-\tfrac{1}{2}(\boldsymbol{\omega}-\boldsymbol{\Omega}(\boldsymbol{a}))^2\}\,[w(\boldsymbol{a},t)+\varepsilon\, y(\boldsymbol{a},\boldsymbol{\omega};w)]\,. \quad (10)$$

Here the correction to the velocity distribution does not depend on time directly:

$$y=-(\boldsymbol{\omega}-\boldsymbol{\Omega})_k\left(\partial_k w-\frac{\Gamma^k_{\text{el.}}}{kT}\,w\right)$$
$$-2(\boldsymbol{\omega}-\boldsymbol{\Omega})_k(\boldsymbol{\omega}-\boldsymbol{\Omega})_l\, w\,\partial_k\,\Omega_l\,, \quad (11)$$

and the distribution function $w(\boldsymbol{a},t)$ obeys the dimensionless equation

$$\dot{w}+\varepsilon\,\partial_k(\Omega_k\,w)=\varepsilon^2\,\partial_k\left(\partial_k w-\frac{\Gamma^k_{\text{el.}}}{kT}\,w\right). \quad (12)$$

This is a kinetic equation for the description of the rotational diffusion of a molecule in external potentials $U(\boldsymbol{a}\cdot\boldsymbol{n})$ and $g^{\alpha\beta}$. The operator $\partial_k=\varepsilon_{kij}\,a_i\,\partial/\partial a_j$ and hence $\Gamma^k_{\text{el.}}=-\partial_k U$. Let us emphasize that the anisotropy of the microscopic friction coefficient λ_{kl} (see (9)) does not contribute to the final equation (12) due to the symmetry properties.

The kinetic equation (12) has been used already by several authors while considering the statistical properties of a flowing nematic (see, for example, [10, 11]). This equation containes only one model parameter – the friction coefficient λ, which is not determined in the theory. Our purpose here is to express it in terms of definite molecular parameters, using the general expression, which follows from the fluctuation-dissipation theorem [15]:

$$\lambda=\frac{1}{3kT}\int_0^\infty \langle\boldsymbol{\Gamma}(t)\cdot\boldsymbol{\Gamma}(0)\rangle_{\text{eq.}}\,\mathrm{d}t, \text{ where } \langle\boldsymbol{\Gamma}\rangle_{\text{eq.}}=0. \quad (13)$$

The Fokker-Planck approximation in the kinetic theory can be used when the stochastic force correlator has a very short relaxation time τ. This time can be estimated as the ratio of the free angular volume fraction per molecule $\Delta\theta$ to the mean velocity of a thermal rotation $\propto\sqrt{kT/I_\perp}$. The free volume $\Delta\theta$ is approximately determined by the molecular dimensions L and d and the number density

$$c=N/V\colon\ \Delta\theta\propto(\sqrt{4/\pi\, c\, L}-d)/L\ll d/L.$$

Now the friction coefficient λ is qualitatively

$$\lambda\cong\tau\langle\Gamma^2(0)\rangle_{\text{eq.}}\cong\Delta\theta\sqrt{I_\perp/kT}\,\langle\Gamma^2(0)\rangle_{\text{eq.}}\,. \quad (14)$$

In the thermodynamical limit the main contribution to the average in (14) is the three-particle correlator

$$\langle\Gamma^2\rangle\cong N^2\int\partial_1\,U(1,2)$$
$$\cdot\,\partial_2\,U(1,3)\,W_3(1,2,3)\,\mathrm{d}(1)\,\mathrm{d}(2)\,\mathrm{d}(3), \quad (15)$$

where $\partial_{1k}=\varepsilon_{kij}\,a_{1i}\,\partial/\partial a_{1j}$, $\mathrm{d}(1)=\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{a}_1$. The usual approximation for the pair intermolecular potential is [16]

$$U(1,2)\cong-\frac{\bar{G}}{r_{12}^6}-\frac{1}{r_{12}^6}\,[\bar{I}_0(\boldsymbol{a}_1\cdot\boldsymbol{a}_2)^2$$
$$+\bar{I}_2(\boldsymbol{a}_1\cdot\boldsymbol{a}_2)(\boldsymbol{a}_1\cdot\boldsymbol{u}_{12})(\boldsymbol{a}_2\cdot\boldsymbol{u}_{12})]\,, \quad (16)$$

where $\boldsymbol{r}_{12}=\boldsymbol{r}_1-\boldsymbol{r}_2=r_{12}\,\boldsymbol{u}_{12}$. Note that the constant $\bar{G}$ in (16) describes the isotropic attraction of molecules while the constants $\bar{I}_0$ and $\bar{I}_2$ determine the anisotropic contribution which is usually smaller; $\bar{I}_0\propto\bar{I}_2\ll\bar{G}$. The steric repulsive part of the intermolecular potential can be taken into account using the step function $\Theta(r_{12}-\xi_{12})$, which excludes the interpenetration of the molecular hard cores and depends on the closest distance of approach for two molecules

$$\xi_{12}\cong d+\frac{L-d}{2}\,[(\boldsymbol{a}_1\cdot\boldsymbol{u}_{12})^2+(\boldsymbol{a}_2\cdot\boldsymbol{u}_{12})^2] \quad \text{(see ref. [16])}.$$

The three-particle angular distribution function, which appears in (15) can be determined firstly using the Kirkwood approximation:

$$W_3(1,2,3)\cong W_2(1,2)\,W_2(1,3)\,W_2(2,3)\,.$$

Neglecting the three-particle collisions, one can transform it to the simple form

$$W_3(1,2,3)\cong\exp\left\{-\frac{U(1,2)}{kT}\right\}\exp\left\{-\frac{U(1,3)}{kT}\right\}$$
$$\cdot\exp\left\{-\frac{U(2,3)}{kT}\right\}w_1(a_1)\,w_1(a_2)\,w_1(a_3). \quad (17)$$

Now we are ready to calculate the integrals in (15) and obtain the estimation of the microscopic friction coefficient of a molecule rotating in the nematic liquid crystal.

As a first step, one should change the variables from $\mathrm{d}\boldsymbol{r}_1, \mathrm{d}\boldsymbol{r}_2, \mathrm{d}\boldsymbol{r}_3$ to $\mathrm{d}\boldsymbol{r}_{12}, \mathrm{d}\boldsymbol{r}_{13}, \mathrm{d}\boldsymbol{r}_3$ and use the saddle point approximation, since the distribution function (17) has a very narrow maximum at 1) minimal $r_{12}=\xi_{12}$, $r_{13}=\xi_{13}$, $r_{23}=\xi_{13}-\xi_{12}$ and 2) minimal $\xi_{12}=\xi_{13}=\xi_{23}=d$, which requires the triangle configuration of $\boldsymbol{u}_{12}$, $\boldsymbol{u}_{13}$ and $\boldsymbol{u}_{23}$, all perpendicular to $\boldsymbol{a}_1$, $\boldsymbol{a}_2$ and $\boldsymbol{a}_3$. As a result of these calculations we obtain

$$\langle \Gamma^2 \rangle \cong c^2 d^6 \frac{\pi d}{L} \frac{I_0^2 \exp(3G/kT)}{(6kT)^3} \tag{18}$$

$$\cdot \int \frac{\partial_1 (\boldsymbol{a}_1 \cdot \boldsymbol{a}_2)^2 \, \partial_1 (\boldsymbol{a}_1 \cdot \boldsymbol{a}_3)^2 \, w_1(1)\, w_1(2)\, w_1(3)\, 4 \exp[I_0((\boldsymbol{a}_1 \cdot \boldsymbol{a}_2)^2 + (\boldsymbol{a}_1 \cdot \boldsymbol{a}_3)^2 + (\boldsymbol{a}_2 \cdot \boldsymbol{a}_3)^2)/kT]}{\sqrt{[G+I_0(\boldsymbol{a}_1 \cdot \boldsymbol{a}_2)^2]\,[G+I_0(\boldsymbol{a}_1 \cdot \boldsymbol{a}_3)^2]}\,[3G+2I_0(\boldsymbol{a}_1 \cdot \boldsymbol{a}_2)^2+I_0(\boldsymbol{a}_2 \cdot \boldsymbol{a}_3)^2]\,[3G+2I_0(\boldsymbol{a}_1 \cdot \boldsymbol{a}_2)^2+I_0(\boldsymbol{a}_2 \cdot \boldsymbol{a}_3)^2]} \, \mathrm{d}\boldsymbol{a}_1 \, \mathrm{d}\boldsymbol{a}_2 \, \mathrm{d}\boldsymbol{a}_3 \,,$$

where the parameters $G=\bar{G}/d^6$ and $I_0=\bar{I}_0/d^6$ (see (16)) have the dimensionality of energy.

The equilibrium one-particle distribution function, which appears in (17) and (18), is determined by the orientation mean-field potential:

$$w_1 \propto \exp(-U(\boldsymbol{a} \cdot \boldsymbol{n})/kT),$$

and $U(\boldsymbol{a}_1 \cdot \boldsymbol{n})$ is simply related to the pair potential $U(\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{r}_{12})$ (16) averaged over the coordinates and orientations of the second molecule. Then the mean-field potential can be written as

$$\begin{aligned} U(\boldsymbol{a}_1 \cdot \boldsymbol{n}) &= c \int U(\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{r}_{12})\, w_1(\boldsymbol{a}_2 \cdot \boldsymbol{n})\, \mathrm{d}\boldsymbol{r}_{12}\, \mathrm{d}\boldsymbol{a}_2 \\ &\cong \mathrm{const} - 2\pi\, \mathrm{d}^3 c (I_2 + \tfrac{2}{3} I_0) \langle P_2 \rangle (\boldsymbol{a}_1 \cdot \boldsymbol{n})^2, \end{aligned} \tag{19}$$

where $\langle P_2 \rangle = S$ is the nematic order parameter and $\boldsymbol{n}$ the director. Now the integration in the (18) can be carried out using again the saddle point approximation, the smallness of the ratio I_0/G and the restriction that the vectors $\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3$ in (18) should form a triangle pyramid with the base similar to the $\boldsymbol{u}_{12}, \boldsymbol{u}_{13}, \boldsymbol{u}_{23}$ triangle and the axis long the $\boldsymbol{n}$ direction. Omitting the complicated details we present here the final estimation for the microscopic friction coefficient λ:

$$\begin{aligned} \lambda &\cong 100(1-\phi)\, c^2 d^6 \left(\frac{d}{L}\right)^2 \frac{(kT)^5}{G^3} \sqrt{I_\perp/kT} \\ &\cdot \exp\left(3\,\frac{G+I_0}{kT}\right), \end{aligned} \tag{20}$$

where the parameter ϕ is the volume fraction of molecules (usually for dense molecular liquids $\phi \propto 0.5$–0.6).

Let us emphasize the mainly isotropic form of the nematic friction coefficient; all anisotropic effects give only small corrections to (20). One could expect this fact, because the nematic and the isotropic phase of a liquid crystal are very similar to each other as far as the local order is concerned. The activation Arrhenius law in the temperature dependence of λ is the other important feature of the (20). Note that the activational energy is determined mainly by the isotropic intermolecular attraction $\bar{G}/r_6^{12}$ (see (16)) and possesses very weak temperature dependence.

Now all parameters of the kinetic equation (12) are determined and one can turn to the phenomenological viscous stress tensor evaluation.

4. The Leslie Coefficients

The macroscopic stress tensor $\hat{\sigma}$ can be calculated by averaging the microscopic tensor $\hat{\sigma}^M$ (see (7)). However, it is convenient to represent the microscopic stress tensor $\hat{\sigma}^M$ as a sum of the symmetrical and antisymmetrical parts: $\hat{\sigma}^M = \hat{\sigma}^M_{\mathrm{s}} + \hat{\sigma}^M_{\mathrm{a}}$, and to average these parts separately. Then the average of the symmetrical part $\langle \hat{\sigma}^M_{\mathrm{s}} \rangle$ can be calculated exactly without solving the Fokker-Planck equation (see [10, 12] for details). Indeed, it is possbile to obtain the explicit expression for $\langle \hat{\sigma}^M_{\mathrm{s}} \rangle$ directly from the Fokker-Planck equation multiplying it with $(a_\alpha a_\beta - \frac{1}{3}\delta_{\alpha\beta})$ and integrating over $\boldsymbol{a}$. The result is

$$\begin{aligned} \langle \hat{\sigma}^M_{\mathrm{s}} \rangle = \frac{ckT}{2\varepsilon} \bigg(\frac{p^2-1}{p^2+1} &[-2\langle P_4 \rangle\, \boldsymbol{nn}(\boldsymbol{nn}\colon \hat{A}) \\ &+ \tfrac{1}{7}(3\langle P_2 \rangle + 4\langle P_4 \rangle)(\boldsymbol{nn} \cdot \hat{A} + \hat{A} \cdot \boldsymbol{nn}) \\ &+ \tfrac{2}{35}(7 - 5\langle P_2 \rangle - 2\langle P_4 \rangle)\, \hat{A}] \\ &+ \langle P_2 \rangle (\boldsymbol{nn} \cdot \hat{g}_{\mathrm{a}} - \hat{g}_{\mathrm{a}} \cdot \boldsymbol{nn}) \bigg), \end{aligned} \tag{21}$$

where $\hat{A}$ and $\hat{g}_{\mathrm{a}}$ are the symmetrical and antisymmetrical parts of the flow velocity gradients $\hat{g}$; the equilibrium averages $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are the nematic order parameters of the second and fourth order, respectively.

Equation (21) determines the part of Leslie coefficients which contributes to the symmetrical part of the expression (1), i.e. $\alpha_1, \alpha_4, \alpha_5+\alpha_6$ and $\alpha_2+\alpha_3=\gamma_2$. On the other hand, the separate calculation of α_2 and α_3 requires the averaging of the antisymmetrical part of microscopic stress tensor $\frac{1}{2}c(a_\alpha \partial U/\partial a_\beta - a_\beta \partial U/\partial a_\alpha)$ with the corresponding nonequilibrium distribution function, which is the solution of (12). At this point the problem can be simplified using symmetry considerations. Indeed, the scalar correction $h_{\mu\varrho} g^{\mu\varrho}$ to the equilibrium Boltzmann distribution in a uniaxial nematic can depend only on the two vectors $\boldsymbol{a}$ and $\boldsymbol{n}$. Let us introduce the pair of orthogonal unit vectors $\boldsymbol{n}$ and $\boldsymbol{e}$ so that $\boldsymbol{a}=\boldsymbol{n}\cos\theta+\boldsymbol{e}\sin\theta$ and write down the above correction in the general form

$$\begin{aligned} h_{\mu\varrho} g^{\mu\varrho} = {} & h_0 n_\mu n_\varrho A^{\mu\varrho} + h_s n_\mu e_\varrho A^{\mu\varrho} \\ & + h_a n_\mu e_\varrho g_a^{\mu\varrho} + h_2 e_\mu e_\varrho A^{\mu\varrho}, \end{aligned} \tag{22}$$

where we suggested that $g^{\alpha\alpha}=0$ (the liquid is incompressible). The scalar functions h_0, h_s, h_a and h_2 can depend only on the polar angle θ because $\cos\theta=(\boldsymbol{a}\cdot\boldsymbol{n})$ is the only possible scalar combination. The averaging over the azimuthal angle φ, determined by the orientation of the vector $\boldsymbol{e}$, can easily be performed, and we obtain for the antisymmetrical part of $\hat{\sigma}^M$

$$\begin{aligned} \sigma_a^{\alpha\beta} = \tfrac{1}{2} c \frac{\partial U}{\partial \theta} & [h_s (n_\alpha n_\beta A^{\mu\beta} - n_\beta n_\mu A^{\mu\alpha}) \\ & - \tfrac{1}{2} h_a (n_\alpha N_\beta - n_\beta N_\alpha)] \end{aligned}$$

(compare with (1)). Therefore the coefficients $\alpha_5-\alpha_6$ and $\gamma_1=\alpha_3-\alpha_2$ are determined by the functions $h_s(\theta)$ and $h_a(\theta)$, respectively. It has been shown [10] that the expression for $\alpha_5-\alpha_6$ can be transformed exactly to $\alpha_2+\alpha_3$, which follows from (21), in agreement with the Parodi relation. The rotational viscosity coefficient γ_1 should be determined separately:

$$\gamma_1 = \frac{c}{2} \int_0^\pi w_0(\theta) \frac{\partial U}{\partial \theta} h_a(\theta) \sin\theta \, d\theta. \tag{23}$$

Now one has only to determine the function $h_a(\theta)$. The kinetic equation for the function $h_a(\theta)$ can be derived from (12) and (22) by substitution of the expression for $\Omega(\hat{g}, \boldsymbol{a})$. In this way one obtains:

$$\frac{\partial^2 h_a}{\partial \theta^2} + \left(\operatorname{ctg}\theta - \frac{\partial U/kT}{\partial \theta} \right) \frac{\partial h_a}{\partial \theta} - \frac{h_a}{\sin^2\theta} = -\frac{1}{\varepsilon} \frac{\partial U/kT}{\partial \theta}. \tag{24}$$

The last term on the left-hand side of the (24) is relatively small if we consider the nematic far from the clearing point. Indeed, all derivatives $\partial/\partial\theta$ have the typical value $q=J/kT \gg 1$, where J denotes the coefficient at $(\boldsymbol{a}\cdot\boldsymbol{n})$ in (19) for the mean field potential $U(\theta)$. If one neglects the term $h/\sin^2\theta$ in comparison with other terms, proportional to q and q^2, (24) becomes very simple:

$$\frac{1}{\sin\theta} e^{U/kT} \frac{\partial}{\partial\theta} \left[e^{-U/kT} \sin\theta \frac{\partial h_a}{\partial \theta} \right] = -\frac{1}{\varepsilon} \frac{\partial U/kT}{\partial \theta}. \tag{25}$$

The neglection of the term $h_a/\sin^2\theta$ corresponds to the fact that the relaxation time of the molecular rotation about the $\boldsymbol{n}$ axis (the angle φ) is much smaller than the time of reorientation with respect to the angle θ, related to the overcoming of the potential barrier (see [17]). So, considering the stationary reorientation process in the g^{kl} field, the distribution function can be considered as being averaged over φ. The solution of (25) cayn be obtained by simple integration:

$$h_a \cong -\frac{1}{\varepsilon} \int_0^\theta \frac{e^{U(x)/kT}}{\sin x} \int_0^x e^{-U(z)/kT} \frac{\partial U(z)/kT}{\partial z} \sin z \, dz \, dx. \tag{26}$$

Now, substituting $h_a(\theta)$ into the expression for γ_1 [(23)], one should perform the corresponding integration

$$\begin{aligned} \gamma_1 \cong -\frac{c}{2\varepsilon Z} \int_0^\pi \frac{\partial U(\theta)}{\partial \theta} e^{-U(\theta)/kT} \sin\theta \int_0^\theta \frac{e^{U(x)/kT}}{\sin x} \\ \cdot \int_0^x e^{-U(z)/kT} \frac{\partial U(z)/kT}{\partial z} \sin z \, dz \, dx \, d\theta, \end{aligned} \tag{27}$$

where the normalization factor

$$Z = 2\pi \int_0^\pi e^{-U/kT} \sin\theta \, d\theta \cong 2\pi/q.$$

In the $q=J/kT \gg 1$ approximation one can use the saddle-point method to execute the integrals in (27). It is clear that the external integral has the saddle point near $\theta=\pi$, in fact at $\theta^* \cong \pi - q^{-1/2}$. The integral over x has the saddle in the point $x^*=\pi/2$ and the internal one in the point $z^* \cong q^{-1/2}$. Evaluating (27) in this sort of sequence we obtain the expression for the Leslie coefficient γ_1, which is asymptotically exact in the limit of large q. Returning to the dimensional variables, γ_1 takes the form

$$\gamma_1 \cong \tfrac{1}{6} c \lambda \sqrt{J/kT} \, e^{J/kT} = \alpha_3 - \alpha_2, \tag{28}$$

where the mean-field coupling constant J has been given by (19): $J \cong 2\pi c d^3 (I_2 + \frac{2}{3} I_0) \langle P_2 \rangle$ *.

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* In our previous paper [17] we have presented preliminary results for the Leslie coefficients. However, in that work we have made a too rough approximation in the calculation of the symmetrical part of the stress tensor. As a result, the six Leslie coefficients become proportional to $\exp(J/kT)$, which is not correct, as one can see here.

Now all six Leslie coefficients can be determined separately: α_1, α_4, $\alpha_2+\alpha_3$ and $\alpha_5+\alpha_6$ from (21); $\alpha_5-\alpha_6=\alpha_2+\alpha_3$ from the Parodi relation and $\alpha_3-\alpha_2=\gamma_1$ from (28). The expressions for $\alpha_1-\alpha_6$ can be written in the following form using only defined molecular parameters

$$\begin{aligned}
\alpha_1 &= -c\lambda \frac{p^2-1}{p^2+1}\langle P_2\rangle, \\
\alpha_2 &= -\frac{c\lambda}{2}S-\tfrac{1}{2}\gamma_1 \cong -\frac{c\lambda}{2}\left[S+\tfrac{1}{6}\sqrt{J/kT}\,e^{J/kT}\right], \\
\alpha_3 &= -\frac{c\lambda}{2}S+\tfrac{1}{2}\gamma_1 \cong -\frac{c\lambda}{2}\left[S-\tfrac{1}{6}\sqrt{J/kT}\,e^{J/kT}\right], \\
\alpha_4 &= \frac{c\lambda}{35}(7-5S-2\langle P_4\rangle), \qquad\qquad (29) \\
\alpha_5 &= \frac{c\lambda}{2}\left[\frac{p^2-1}{p^2+1}\tfrac{1}{7}(3S+4\langle P_4\rangle)+S\right], \\
\alpha_6 &= \frac{c\lambda}{2}\left[\frac{p^2-1}{p^2+1}\tfrac{1}{7}(3S+4\langle P_4\rangle)-S\right],
\end{aligned}$$

where $S=\langle P_2\rangle$ and λ is givn by (20).

5. Discussion

In this paper we have considered the Brownian motion of a molecule in a flowing nematic liquid crystal and derived the Fokker-Planck equation for the one-particle distribution function in the case of an arbitrary velocity gradients tensor. It should be noted that we have used the very simple model for a nematic liquid crystal, i.e. a system of cylindrically symmetric rod-like particles which interact via the mean field potential. However, this is the first necessary step in the development of a consistent molecular theory for the rheological properties of liquid crystals. Then the most interesting question, which arises here, is which properties of the viscous coefficients, observed in real nematics, can be described with the help of this simple model. One can conclude that these basic properties should correspond to any thermotropic nematic, composed of elongated molecules, regardless the particular molecular structure.

The main results of the present paper are the expressions (29) for the Leslie coefficients. Note that (29) is similar to the corresponding expressions obtained by Kuzuu and Doi (see (6.2) of [10]). However, our development of the theory has lead to a more detailed description of the liquid crystal viscosity. Firstly, the microscopic friction coefficient λ has been expressed in terms of the molecular model parameters (see (20)) and, secondly, an explicit expression for the rotational viscosity γ_1 has been obtained. These new results have a significant influence on the general description of Leslie coefficients. Indeed, according to (20) the friction coefficient λ posesses the exponential temperature dependence which is mainly responsible for the experimentally observed temperature variation of Leslie coefficients. At the same time, the temperature variation of the rotational viscosity γ_1 is characterized by an additional exponential term with a smaller activation energy determined by the mean field potential barrier.

The estimation of the mean-field coupling constant J can be obtained from the Maier and Saupe theory: $J \simeq J_0 S$ and $J_0 \simeq 4.5\,kT_c$, where T_c is the clearing temperature (see (19)). It is easy to check that $(J/kT)^{1/2}e^{J/kT} > 6S$ within the whole range of the nematic phase. Therefore $\alpha_2<0$, $\alpha_3>0$ and $|\alpha_2| \gg \alpha_3$. The parameter $(p^2-1)/(p^2+1)$ is positive and smaller than unit in the case of elongated molecules. Hence $\alpha_5>0$, $\alpha_6<0$ and $\alpha_5 \gg |\alpha_6|$. One can note also that $|\alpha_1| \ll |\alpha_2| \propto \alpha_4 \propto \alpha_5$. Thus the main qualitative features of Leslie coefficients obtained in this model correspond to the experimental data.

All Leslie coefficients are proportional to the microscopic friction coefficient λ, which determines the activational temperature dependence of α's. Let us note that the main contribution to the activational energy E_{act} is proportional to the isotropic coupling constant: $E_{act} \simeq 3G \gg J$. It can be estimated using the results of the direct quantum chemical calculations of the intermolecular interaction energy for typical nematics [18, 19], and the results is: $G \simeq (5 \div 10)J$. Thus the activation energy, estimated within the present theory, corresponds to typical experimental values $E_{act} \simeq E_1 + E_2 S$ (see [2]), with $E_1 \simeq 0{,}5\,eV$ and $E_2 \ll E_1$. Let us note also that the ratio of any two Leslie coefficients does not depend on λ. Then the ratio of the rotational viscosity γ_1 to γ_2 (or any other viscosity coefficient) would show a weaker temperature variation with an activation energy $E_2 \simeq J_0 S$. This conclusion can be verified experimentally. It is interesting also that within the present theory the γ_1 to γ_2 ratio is determined only by the nematic order parameter S.

The additional activational exponent in the coefficient γ_1 arises from the process of the overcoming of the potential barrier by a molecule, which rotates in the mean field potential $U(\boldsymbol{a} \cdot \boldsymbol{n})$. This result corresponds to the Diogo and Martins idea. However, their subsequent suggestion that the same factor determines all Leslie coefficients appears to be uncorrect.

The results of the present theory are not limited to the Leslie coefficients. Indeed, the kinetic equation for the one-particle distribution function of the flowing system and its stationary solution can be used in the calculations of other kinetic coefficients, for example thermoconductivity. The non-stationary solution of this equation can yield different relaxation times which are necessary for the description of various spectroscopic experiments. And, finally, the general approach developed here can be applied to other anisotropic fluid systems such as discotics or polymers.

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