Viscous properties of binary mixtures of nematic liquid crystals

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(Received 9 June 1995)

Viscous properties of binary mixtures of nematic liquid crystals have been investigated on the basis of the mean field potential approximation. Rotational diffusion coefficients of components are discussed. The Leslie viscosity coefficients for binary mixture have been calculated using the Doi approach.

PACS number(s): 61.30.−v, 66.20.+d, 64.75.+g

I. INTRODUCTION

Viscosity coefficients, due to their importance in the design of liquid-crystal materials, are the subject of intensive studies. In particular, in electro-optic applications, the rotational viscosity coefficient γ_1 is a very important quantity, because the response time of liquid-crystal devices is proportional to its value. Hence materials with prescribed parameters are needed in many technical applications. On the other hand, it is often hard to find chemically pure nematic substances possessing desired features. Thus, one has to employ mixtures of nematic materials.

Existing theories, describing the viscous properties of pure nematic liquid crystals seem to be satisfactory. Unfortunately, an analogous theory concerning mixtures is still missing. It is obvious that such a theory, which would allow us to predict properties of mixtures, would be very useful in technical applications.

Reference [1] presents the microscopic theory of binary mixtures of uniaxial nematic liquid crystals. Authors, starting from the Bogoliubov-Born-Green-Kirkwood-Yvon hierarchy equations, have obtained systems of self-consistent equations for the equilibrium one-particle distribution functions. The appropriate free-energy functional and stability conditions are also discussed in detail.

In this paper we investigate the viscous properties of binary mixtures in the framework of the microscopic theory presented in [1]. We make an attempt at expressing the viscosity coefficients in terms of molecular parameters characterizing pure components. We adopt the Doi [2] method for a system consisting of two kinds of nematic molecules. We obtain a microscopic stress tensor for mixtures in the mean-field approximation. Next, comparing it with appropriate phenomenological Ericsen-Leslie formulas, we derive microscopic expressions for the six Leslie viscosity coefficients.

II. THE KINETIC EQUATION FOR BINARY MIXTURES

We consider a spatially homogeneous system composed of two kinds of uniaxial molecules, A and B, under the influence of a low velocity gradient field. The probability that at time t the long axes of two arbitrary molecules of types A and B point to the direction of $\mathbf{u}_A$ and $\mathbf{u}_B$, respectively, is described by the orientational distribution function $f(\mathbf{u}_A, \mathbf{u}_B; t)$. We assume that the motion of a selected molecule in a solution can be treated as a rotational Brownian motion in a certain external mean potential, which is different for molecules of type A and B. The standard method used for one-component systems was described in Refs. [3,4]. For the two-component system we propose the following Fokker-Planck equation governing the time evolution of $f(\mathbf{u}_A, \mathbf{u}_B; t)$:

$$\frac{\partial f}{\partial t} = D_A \mathcal{R}_A \left(\mathcal{R}_A f - \frac{f}{kT} \mathcal{R}_A V^A[f] \right) + D_B \mathcal{R}_B \left(\mathcal{R}_B f - \frac{f}{kT} \mathcal{R}_B V^B[f] \right) - \mathcal{R}_A \omega_{\mathbf{A}} f - \mathcal{R}_B \omega_{\mathbf{B}} f + 2 D_{AB} \mathcal{R}_A \mathcal{R}_B f \ , \tag{1}$$

where $\mathcal{R}_A$ and $\mathcal{R}_B$ are the differential operators $\mathbf{u}_A \times \partial/\partial \mathbf{u}_A$ and $\mathbf{u}_B \times \partial/\partial \mathbf{u}_B$, respectively. The first two terms on the right side of the above equation represent the Brownian motion in the presence of the mean potentials V^A and V^B, respectively. Here D_A and D_B are the effective rotational diffusion coefficients in the solution of particles A and B. The next two terms represent the effect of the velocity gradient, which rotates each molecule with a certain average angular velocity ω. For an ellipsoidal molecule with the long axis parallel to the unit vector $\mathbf{u}$, characterized by the length to width ratio p, it has the form [5]

$$\omega = \frac{p^2 - 1}{p^2 + 1} \mathbf{u} \times (\hat{\mathbf{A}} \cdot \mathbf{u}) - \mathbf{u} \times (\hat{\mathbf{\Omega}} \cdot \mathbf{u}), \tag{2}$$

where $\hat{\mathbf{A}}$ and $\hat{\mathbf{\Omega}}$ are the symmetric and antisymmetric parts of the flow velocity gradient:

$$A_{\alpha\beta} = \tfrac{1}{2}(\partial_\alpha v_\beta + \partial_\beta v_\alpha), \quad \Omega_{\alpha\beta} = \tfrac{1}{2}(\partial_\alpha v_\beta - \partial_\beta v_\alpha) \ . \tag{3}$$

Naturally, because of the different p ratio, the average angle velocities of A- and B-type molecules are different. Finally, the last term in (1) is due to the correlation in chaotic motion of two kinds of molecules. In general case

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there is no reason to omit it. In this paper, however, we assume that in the equilibrium (in absence of velocity gradient) the orientational distribution function f_0 is a product of two one-particle orientational distribution functions

$$f_0(\mathbf{u}_A, \mathbf{u}_B) = f_0^A(\mathbf{n}\cdot\mathbf{u}_A) f_0^B(\mathbf{n}\cdot\mathbf{u}_B), \tag{4}$$

where $\mathbf{n}$ is an arbitrary unit vector. Under this assumption the cross-diffusion coefficient D_{AB} ($D_{AB} = D_{BA}$) is defined as

$$D_{AB} = \frac{d}{dt}\langle \mathbf{u}_A(0)\cdot\mathbf{u}_B(t)\rangle = \frac{d}{dt}\langle \mathbf{u}_A(0)\rangle\cdot\langle \mathbf{u}_B(t)\rangle,$$

where $\langle\,\rangle$ denotes the equilibrium average and vanishes for the steady-state solution.

In the kinetic equation (1), two phenomenological constants D_A and D_B appear whose values are not determined within the framework of our theory. Moreover, both these diffusion coefficients are nontrivial functions depending on the temperature and the concentration of the two components A and B. In the case of one-component nematic liquid crystals the diffusion constant can be successfully incorporated into theory from experiment [6]. Unfortunately, for mixtures this problem is much more complicated. The point is that there are no analogous experimental data that would allow us to establish two rotational diffusion constants in mixtures independently. Hence, we have to calculate both coefficients on the basis of existing experimental data, where the properties of pure nematic materials are taken into account.

In the next section we show the method that allows us to calculate the temperature dependence of both rotational diffusion coefficients for arbitrary molar fractions of components.

III. THE ROTATIONAL DIFFUSION COEFFICIENTS OF COMPONENTS OF A BINARY MIXTURE

According to the fluctuation-dissipation theorem the rotational friction coefficient ξ, related to the rotational diffusion coefficient D by Einstein's formula, $D = kT/\xi$, is given by the following average:

$$\xi = \frac{1}{3kT}\int_0^\infty \langle\Gamma(0)\Gamma(t)\rangle\, dt, \quad \langle\Gamma\rangle = 0 \tag{5}$$

where $\Gamma(t)$ is the total torque exerted on the selected molecule at time t by the surrounding molecules and $\langle\,\rangle$ denotes the equilibrium average. We can assume that the time correlation function, $\langle\Gamma(0)\Gamma(t)\rangle$, which appears in Eq. (5), decays exponentially with very short relaxation time τ. This is a direct consequence of the Fokker-Planck approximation, which is assumed to be valid for the considered system. We have

$$\int_0^\infty \langle\Gamma(0)\Gamma(t)\rangle dt \approx \left\langle\Gamma^2(0)\right\rangle \int_0^\infty e^{-t/\tau} dt = \tau\left\langle\Gamma^2(0)\right\rangle. \tag{6}$$

The estimation of τ is given by the formula

$$\tau = \Delta\Theta\sqrt{\frac{I}{kT}}, \tag{7}$$

where I is the transverse moment of inertia of a molecule and $\Delta\Theta$ is the free angular volume fraction per molecule. For estimation of $\Delta\Theta$ we use the following expression [4,8,9]:

$$\Delta\Theta = (a - 2\nu r)/L, \tag{8}$$

where r and L are the radius and the length of a molecule, ν is a certain numerical factor, and a is a functional depending, in the general case, on the one-particle orientational distribution function, number of molecules in unit volume, and length L. Although estimation (8) has been calculated for one-component systems, we expect that its validity can be successfully extended for binary mixtures. Such a generalization seems to be especially reasonable when a mixture of two similar kinds of molecules is under consideration.

One can check that by applying relation (5) for a two-component system we obtain:

$$\xi_A = \frac{\tau_A}{3kT}\left[d_A^2\mathcal{I}_{A,A}^A + d_B^2\mathcal{I}_{B,B}^A + 2d_Ad_B\mathcal{I}_{A,B}^A\right], \tag{9}$$
$$\xi_B = \frac{\tau_B}{3kT}\left[d_B^2\mathcal{I}_{B,B}^B + d_A^2\mathcal{I}_{A,A}^B + 2d_Bd_A\mathcal{I}_{B,A}^B\right],$$

where d_A and d_B are the number densities of components A and B, respectively, $\tau_A = \Delta\Theta_A\sqrt{I_A/kT}$, $\tau_B = \Delta\Theta_B\sqrt{I_B/kT}$, and integrals $\mathcal{I}_{I,J}^K$ are defined as follows:

$$\mathcal{I}_{I,J}^A = \int \partial_1 V^{A,I}(1,2)\partial_1 V^{A,J}(1,3) \times f_3^{A,I,J}(1,2,3)d(1)d(2)d(3), \tag{10}$$
$$\mathcal{I}_{I,J}^B = \int \partial_1 V^{B,I}(1,2)\partial_1 V^{B,J}(1,3) \times f_3^{B,I,J}(1,2,3)d(1)d(2)d(3).$$

Here ∂_1 denotes the spheric derivative, $\mathbf{n_1}\times\partial/\partial\mathbf{n_1}$, and $V^{A,I}$ and $V^{B,I}$ are the interaction potentials between an appropriate pair of molecules. $f_3^{K,I,J}(1,2,3)$ is the three-particle distribution function describing the probability that the position of molecules of K, I, and J type is given by (1), (2), and (3), respectively [we use the abbreviation $(\mathbf{i}) \equiv (\mathbf{r_i}, \mathbf{n_i})$].

Formulas (7)–(10) allow us to express both constants D_A and D_B in terms of quantities characterizing the pure components. For further calculation, however, knowledge of the explicit form of all interaction potentials $V^{A,A}$, $V^{B,B}$, and $V^{A,B}$ is needed. Therefore, the problem of the rotational diffusion coefficients will be not discussed in detail in this paper.

IV. THE STRESS TENSOR

In general, the theory of dissipative systems is determined by the viscous stress tensor $\hat{\sigma}$. The hydrodynamics of nematic liquid crystals in the absence of external fields is given by two constitutive equations proposed by Ericsen and Leslie:

$$\sigma_{\alpha\beta} = \alpha_1 n_\alpha n_\beta n_\mu n_\varrho A_{\mu\varrho} + \alpha_4 A_{\alpha\beta} + \alpha_5 n_\alpha n_\mu A_{\mu\beta} + \alpha_6 n_\beta n_\mu A_{\mu\alpha} + \alpha_2 n_\alpha N_\beta + \alpha_3 n_\beta N_\alpha, \tag{11}$$
$$0 = \mathbf{n}\times(\mathbf{h} - \gamma_1\mathbf{N} - \gamma_2\hat{\mathbf{A}}\cdot\mathbf{n}), \tag{12}$$

where

$$\mathbf{N} = \frac{d\mathbf{n}}{dt} + \hat{\mathbf{\Omega}}\cdot\mathbf{n}\,,\ \gamma_1 = \alpha_3 - \alpha_2\,,\ \gamma_2 = \alpha_6 - \alpha_5\,. \tag{13}$$

$\hat{\mathbf{A}}$ and $\hat{\mathbf{\Omega}}$ are defined in (3) and the constants $\alpha_1, \ldots, \alpha_6$ are called Leslie coefficients. Here, $\mathbf{h}$ denotes the molecular field, which is in an equilibrium state parallel to the director $\mathbf{n}$. It is obvious that the above phenomenological equations are valid as well in the theory of mixture of nematic liquid crystal molecules as long as only one common director field $\mathbf{n}(\mathbf{r})$ is present. In this section we make use of the first Ericsen-Leslie equation, and derive the symmetric part of the viscous stress tensor in terms of molecular parameters. In the next section, using the second one, we obtain the antisymmetric part.

In order to obtain the desired expression for the microscopic stress tensor we follow the standard procedure [4] and analyze the change in the free energy caused by the small velocity gradient field. The stress tensor $\epsilon_{\alpha\beta}$ fulfills the following relation:

$$\delta\mathcal{F} = \sigma_{\alpha\beta}\epsilon_{\alpha\beta} + O(\hat{\epsilon}^2), \tag{14}$$

where $\hat{\epsilon}$ denotes a hypothetical small deformation tensor.

The free energy $\mathcal{F}$ per unit volume of the binary system is expressed as [1]

$$\begin{aligned}\mathcal{F} = {} & d_A kT \int f^A(\mathbf{u}) \ln[f^A(\mathbf{u})] d^2\mathbf{u} + d_B kT \int f^B(\mathbf{u}) \ln[f^B(\mathbf{u})] d^2\mathbf{u} \\ & -\frac{1}{2} d_A^2 \int K^{AA}(\mathbf{u}_1, \mathbf{u}_2) f^A(\mathbf{u}_1) f^A(\mathbf{u}_2) d^2\mathbf{u}_1 d^2\mathbf{u}_2 - \frac{1}{2} d_B^2 \int K^{BB}(\mathbf{u}_1, \mathbf{u}_2) f^B(\mathbf{u}_1) f^B(\mathbf{u}_2) d^2\mathbf{u}_1 d^2\mathbf{u}_2 \\ & -d_A d_B \int K^{AB}(\mathbf{u}_1, \mathbf{u}_2) f^A(\mathbf{u}_1) f^B(\mathbf{u}_2) d^2\mathbf{u}_1 d^2\mathbf{u}_2,\end{aligned} \tag{15}$$

where $f^A(\mathbf{u})$ and $f^B(\mathbf{u})$ are the one-particle orientational distribution functions normalized to unity, and d_A and d_B denote number densities of particles A and B, respectively. In general, integral kernels K^{AA}, K^{BB}, and K^{AB}, related to the interaction energy between appropriate pairs of molecules, are quite general functions of two vectors, $\mathbf{u}_1$ and $\mathbf{u}_2$. Their generality is limited by interaction symmetry. We do not restrict ourselves to potentials, which depend only on the inner product $\mathbf{u}_1 \cdot \mathbf{u}_2$. The change $\delta\mathcal{F}$ in the free energy due to the small variations δf^A and δf^B has the form

$$\begin{aligned}\delta\mathcal{F} = {} & d_A kT \int \delta f^A(\mathbf{u}) d^2\mathbf{u} + d_A kT \int \delta f^A(\mathbf{u}) \ln(f_0^A)(\mathbf{u}) d^2\mathbf{u} \\ & + d_B kT \int \delta f^B(\mathbf{u}) d^2\mathbf{u} + d_B kT \int \delta f^B(\mathbf{u}) \ln[f_0^B(\mathbf{u})] d^2\mathbf{u} - d_A \int \left(V^{AA}[f_0^A, \mathbf{u}] + V^{AB}[f_0^B, \mathbf{u}]\right) \delta f^A(\mathbf{u}) d^2\mathbf{u} \\ & - d_B \int \left(V^{BB}[f_0^B, \mathbf{u}] + V^{BA}[f_0^A, \mathbf{u}]\right) \delta f^B(\mathbf{u}) d^2\mathbf{u},\end{aligned} \tag{16}$$

where

$$\begin{aligned}V^{AA}[\varphi, \mathbf{u}] &= d_A \int K^{AA}(\mathbf{u}_1, \mathbf{u}) \varphi(\mathbf{u}_1) d^2\mathbf{u}_1, \\ V^{AB}[\varphi, \mathbf{u}] &= d_B \int K^{AB}(\mathbf{u}_1, \mathbf{u}) \varphi(\mathbf{u}_1) d^2\mathbf{u}_1, \\ V^{BB}[\varphi, \mathbf{u}] &= d_B \int K^{BB}(\mathbf{u}_1, \mathbf{u}) \varphi(\mathbf{u}_1) d^2\mathbf{u}_1, \\ V^{BA}[\varphi, \mathbf{u}] &= d_A \int K^{AB}(\mathbf{u}_1, \mathbf{u}) \varphi(\mathbf{u}_1) d^2\mathbf{u}_1,\end{aligned}$$

Hereafter we will omit in notation the dependence of the above functionals on the director $\mathbf{u}$.

In the velocity gradient field each molecule rotates with the average angular velocity ω given by (2) and in the infinitesimal time δt it changes its orientation by a small angle $\delta\mathbf{\Theta}$,

$$\delta\mathbf{\Theta} = \delta\mathbf{u} \times \frac{(p^2\hat{\epsilon} - \hat{\epsilon}^\dagger) \cdot \mathbf{u}}{p^2 + 1}, \tag{17}$$

where $\epsilon_{\alpha\beta} = \partial_\beta v_\alpha \, \delta t$ can be treated as a hypothetical small deformation tensor. Therefore we can express both variations δf^A and δf^B, which are assumed to be linear in $\hat{\epsilon}$, as

$$\delta f^A = -\delta\mathbf{\Theta}_A \mathcal{R}_A f_0^A, \quad \delta f^B = -\delta\mathbf{\Theta}_B \mathcal{R}_B f_0^B. \tag{18}$$

Substituting (17) and (18) into (16) and using a similar technique as in [2,7] we obtain the following expressions for symmetric and antisymmetric parts of the microscopic stress tensor:

$$\begin{aligned}\langle\hat{\sigma}_{\text{micr}}^{\text{sym}}\rangle = {} & 3kTd_A f(p_A)\left(\mathbf{u}_A\mathbf{u}_A - \frac{1}{3}\hat{I}\right) + \frac{d_A}{2}\left(\mathbf{u}_A(\mathbf{u}_A \times \mathcal{R}_A V_0^A) + (\mathbf{u}_A \times \mathcal{R}_A V_0^A)\mathbf{u}_A\right) \\ & + 3kTd_B f(p_B)\left(\mathbf{u}_B\mathbf{u}_B - \frac{1}{3}\hat{I}\right) + \frac{d_B}{2}\left[\mathbf{u}_B(\mathbf{u}_B \times \mathcal{R}_B V_0^B) + (\mathbf{u}_B \times \mathcal{R}_B V_0^B)\mathbf{u}_B\right],\end{aligned} \tag{19}$$

$$\langle\hat{\sigma}_{\text{micr}}^{\text{asym}}\rangle = \frac{d_A}{2}\left[\mathbf{u}_A(\mathbf{u}_A \times \mathcal{R}_A V_0^A) - (\mathbf{u}_A \times \mathcal{R}_A V_0^A)\mathbf{u}_A\right] + \frac{d_B}{2}\left[\mathbf{u}_B(\mathbf{u}_B \times \mathcal{R}_B V_0^B) - (\mathbf{u}_B \times \mathcal{R}_B V_0^B)\mathbf{u}_B\right], \tag{20}$$

where

$$V_0^A = V^{AA}[f_0^A] + V^{AB}[f_0^B], \quad V_0^B = V^{BB}[f_0^B] + V^{BA}[f_0^A], \tag{21}$$

and

$$f(p) = \frac{p^2-1}{p^2+1}. \tag{22}$$

In order to derive the first phenomenological Ericsen-Leslie equation for the symmetric part of the stress tensor we adopt the method introduced by Kuzuu and Doi [2]. As a result we obtain

$$\begin{aligned}\frac{2}{kT}\hat{\sigma}^{\rm sym} = &-2\left(\frac{d_A}{D_A}f(p_A)^2S_4^A + \frac{d_B}{D_B}f(p_B)^2S_4^B\right)(\hat{\mathbf{A}}:\mathbf{nn})\mathbf{nn}\\ &+2\left(f(p_A)\frac{d_AS_2^A}{D_A} + f(p_B)\frac{d_BS_2^B}{D_B}\right)(\mathbf{nN}+\mathbf{Nn})\\ &+\frac{2}{35}\left(\frac{d_A}{D_A}f(p_A)^2(7-5S_2^A-2S_4^A) + \frac{d_B}{D_B}f(p_B)^2(7-5S_2^B-2S_4^B)\right)\hat{\mathbf{A}}\\ &+\frac{2}{7}\left(\frac{d_A}{D_A}f(p_A)^2(3S_2^A+4S_4^A) + \frac{d_B}{D_B}f(p_B)^2(3S_2^B+4S_4^B)\right)(\hat{\mathbf{A}}\cdot\mathbf{nn}+\mathbf{nn}\cdot\hat{\mathbf{A}}),\end{aligned} \tag{23}$$

where S_2 and S_4 are the equilibrium averages of Legendre's polynomials of second and fourth order.

V. FLOW ALIGNMENT FOR BINARY MIXTURE

In this section we show the way to determine the common director $\mathbf{n}$ of binary mixture effected by the velocity gradient field. Our purpose is also to obtain the second phenomenological equation (12) of the Ericsen-Leslie theory in terms of microscopic quantities of molecules A and B. Following the idea of Kuzuu and Doi [2] we start from the kinetic equation (1) for the steady-state orientational distribution function $f(\mathbf{u}_A,\mathbf{u}_B)$. In our problem a low velocity gradient is assumed. Thus, we use the perturbation method and expand f into series: $f = f_0 + f_1 + \cdots$. The zeroth-order term f_0 is the equilibrium solution, written as $f_0^Af_0^B$. The next term, f_1, takes the form $f_1 = f_0^Af_1^B + f_0^Bf_1^A$, where f_1^A and f_1^B are the first-order perturbations of f_0^A and f_0^B, respectively. Thus, neglecting all higher perturbation terms we have

$$f = f_0^Af_0^B + f_1^Af_0^B + f_1^Bf_0^A. \tag{24}$$

If we make the right-hand side of (1) equal to zero and substitute expression (24) for f we obtain the following system of two equations corresponding to zeroth- and first-order terms, respectively:

$$D_Af_0^B\mathcal{R}_A(\mathcal{R}_Af_0^A - f_0^A\mathcal{R}_A\beta V_0^A + D_Bf_0^A\mathcal{R}_B)\mathcal{R}_Bf_0^B - f_0^B\mathcal{R}_B\beta V_0^B = 0. \tag{25}$$

$$D_Af_0^B\mathcal{G}_A[f_1^A,f_1^B] + D_Bf_0^A\mathcal{G}_B[f_1^A,f_1^B] - f_0^B\mathcal{R}_A\omega_Af_0^A - f_0^B\mathcal{R}_A\omega_Af_0^A = 0, \tag{26}$$

where

$$\begin{aligned}\mathcal{G}_A[f_1^A,f_1^B] &= \mathcal{R}_A(\mathcal{R}_Af_1^A - f_1^A\mathcal{R}_A\beta V_0^A) - f_0^A\mathcal{R}_A\beta(V^{AA}[f_1^A] + V^{AB}[f_1^B]),\\ \mathcal{G}_B[f_1^A,f_1^B] &= \mathcal{R}_B(\mathcal{R}_Bf_1^B - f_1^B\mathcal{R}_B\beta V_0^B) - f_0^B\mathcal{R}_B\beta(V^{BA}[f_1^A] + V^{BB}[f_1^B]),\end{aligned}$$

and $\beta = \frac{1}{kT}$.

Equation (26) has a complicated form. It appears that we can rewrite it after some calculation as

$$\hat{\mathbf{O}}\mathbf{f_1} = \mathbf{w}, \tag{27}$$

where $\mathbf{f_1}$ and $\mathbf{w}$ are two-dimensional vectors. Components of $\mathbf{f_1}$ are functions f_1^A and f_1^B, vector $\mathbf{w}$ is defined as follows:

$$\mathbf{w} = C\begin{pmatrix} C_Af_0^A \\ C_Bf_0^B\end{pmatrix} + \begin{pmatrix} \frac{C_A}{D_A}\mathcal{R}_A\omega_{\mathbf{A}}f_0^A \\ \frac{C_B}{D_B}\mathcal{R}_B\omega_{\mathbf{B}}f_0^B\end{pmatrix},$$

where C, C_A, and C_B are arbitrary constants. Elements of the linear matrix functional $\hat{\mathbf{O}}$ are defined as

$$\begin{aligned}O_{11}[\varphi] &= C_A\mathcal{R}(\mathcal{R}\varphi - \varphi\mathcal{R}\beta V_0^A - f_0^A\beta V^{AB}[\varphi]),\\ O_{12}[\varphi] &= C_A\mathcal{R}f_0^A\mathcal{R}\beta V^{AB}[\varphi],\\ O_{21}[\varphi] &= C_B\mathcal{R}f_0^B\mathcal{R}\beta V^{BA}[\varphi],\\ O_{22}[\varphi] &= C_B\mathcal{R}(\mathcal{R}\varphi - \varphi\mathcal{R}\beta V_0^B - f_0^A\beta V^{BA}[\varphi]).\end{aligned}$$

We look for the solution of Eq. (27) in the form of the infinite series

$$\mathbf{f_1} = \sum_n a_n\mathbf{\Phi_n},$$

where $\mathbf{\Phi_n}$ are right-side eigenvectors of the operator $\hat{\mathbf{O}}$ composed of Φ_n^A and Φ_n^B:

$$\hat{\mathbf{O}}\mathbf{\Phi_n} = \lambda_n\mathbf{\Phi_n}. \tag{28}$$

Let us define the left-side eigenvectors $\mathbf{\Psi_n^\dagger} = (\Psi_n^A, \Psi_n^B)$:

$$\mathbf{\Psi}^\dagger{}_n\hat{\mathbf{O}}^\dagger = \lambda_n\mathbf{\Psi_n^\dagger}. \tag{29}$$

Of course we can normalize eigenvectors in a such way that the orthogonality and normalization condition are fulfilled:

$$\langle\mathbf{\Psi_m^\dagger},\mathbf{\Phi_n}\rangle = \langle\Psi_m^A,\Phi_n^A\rangle + \langle\Psi_m^B,\Phi_n^B\rangle = \delta_{m\,n}, \tag{30}$$

where

$$\langle\Psi_n^A,\Phi_n^A\rangle = \int\Psi_n^A(\mathbf{u_A})\Phi_n^A(\mathbf{u_A})d^2\mathbf{u}_A,$$

$$\langle\Psi_n^B,\Phi_n^B\rangle = \int\Psi_n^B(\mathbf{u_B})\Phi_n^B(\mathbf{u_B})d^2\mathbf{u}_B.$$

We obtain

$$a_n\lambda_n = C\left(\langle\Psi_n^A\rangle\frac{C_A}{D_A} + \langle\Psi_n^B\rangle\frac{C_B}{D_B}\right) + \left(\langle\mathcal{R}_A\omega_{\mathbf{A}}\Psi_n^A\rangle\frac{C_A}{D_A} + \langle\mathcal{R}_B\omega_{\mathbf{B}}\Psi_n^B\rangle\frac{C_B}{D_B}\right). \tag{31}$$

Here $\langle\,\rangle$ denotes the equilibrium average. The equilibrium distribution function $f_0(\mathbf{nu}_A,\mathbf{nu}_B)$ is degenerated. This indicates that for arbitrary rotation of director $\mathbf{n}$ by a small angle $\mathbf{\Theta}$, which changes $\mathbf{n}$ to $\mathbf{n}' \approx \mathbf{n} + \mathbf{n}\times\mathbf{\Theta}$, the function

$$f_0(\mathbf{n}'\mathbf{u}_A,\mathbf{n}'\mathbf{u}_B) \approx f_0(\mathbf{nu}_A,\mathbf{nu}_B) - \mathbf{\Theta}\mathcal{R}^{(n)}f_0(\mathbf{nu}_A,\mathbf{nu}_B) \tag{32}$$

still satisfies Eq. (25). Thus, using the relations $\mathcal{R}_Af =$

$-\mathcal{R}^{(n)}f$, $\mathcal{R}_B f = -\mathcal{R}^{(n)}f$, we have

$$\hat{\mathbf{O}}\begin{pmatrix}\mathbf{\Theta}\mathcal{R}_A f_0^A\\ \mathbf{\Theta}\mathcal{R}_B f_0^B\end{pmatrix} = \mathbf{0}.$$

This means that we have the eigenvalue $\lambda_0 = 0$ for $\Phi_0^A = \mathbf{\Theta}\mathcal{R}_A f_0^A$ and $\Phi_0^B = \mathbf{\Theta}\mathcal{R}_B f_0^B$. One remark is in order: if we leave only the first term in the expansion of $\mathbf{f_1}$, corresponding to the eigenvalue λ_0, then $f = (\mathbf{1} + \mathbf{\Theta}\mathcal{R}^{(n)})f_0$. This means that perturbation removes only the degeneration of the equilibrium solution. Thus, the expansion (24) represents the function f_0 rotated by the small angle $\mathbf{\Theta}$. We are not interested in properties of the steady-state solution.

We analyze the Fokker-Planck equation (1) for the purpose of coming up with information about the antisymmetric part of the stress tensor. In fact, our task has nothing in common with the nonequilibrium problem.

It is obvious that the solvability condition for Eq. (27) reads

$$0 = C\left(\langle\Psi_0^A\rangle\frac{C_A}{D_A} + \langle\Psi_0^B\rangle\frac{C_B}{D_B}\right) + \left(\langle\mathcal{R}_A\omega_{\mathbf{A}}\Psi_0^A\rangle\frac{C_A}{D_A} + \langle\mathcal{R}_B\omega_{\mathbf{B}}\Psi_0^B\rangle\frac{C_B}{D_B}\right). \quad (33)$$

The above relation is an equation that determines the common director $\mathbf{n}$. For further calculation we have to know both eigenvectors Ψ_0^A and Ψ_0^B. We find them in the following way.

Let us define two vectors $\mathbf{x}$ and $\mathbf{y}$ as follows:

$$\mathbf{x}^\dagger = (\Psi_0^A, \Psi_0^B), \quad \mathbf{y} = \begin{pmatrix} f_0^A\\ f_0^B\end{pmatrix}.$$

We have

$$\begin{aligned}\langle\mathbf{x}^\dagger\hat{\mathbf{O}}^\dagger,\mathbf{y}\rangle = &\left\langle f_0^A, \frac{1}{f_0^A}\mathcal{R}_A(f_0^A\mathcal{R}_A\Psi_0^A)\right\rangle\\ &+\left\langle f_0^B, \frac{1}{f_0^B}\mathcal{R}_B(f_0^B\mathcal{R}_B\Psi_0^B)\right\rangle\\ &+\langle f_0^A, \beta V^A[\mathcal{R}_A(f_0^A\mathcal{R}_A\Psi_0^A), \mathcal{R}_B(f_0^B\mathcal{R}_B\Psi_0^B)]\rangle\\ &+\langle f_0^B, \beta V^B[\mathcal{R}_A(f_0^A\mathcal{R}_A\Psi_0^A), \mathcal{R}_B(f_0^{\bar{B}}\mathcal{R}_B\Psi_0^{\bar{B}})]\rangle.\end{aligned}$$

One can check that condition $\mathbf{x}^\dagger\hat{\mathbf{O}}^\dagger = \mathbf{0}$ leads to

$$\mathcal{R}_A(f_0^A\mathcal{R}_A\Psi_0^A) = \mathbf{\Theta}\mathcal{R}_A f_0^A, \quad (34)$$

$$\mathcal{R}_B(f_0^B\mathcal{R}_B\Psi_0^B) = \mathbf{\Theta}\mathcal{R}_B f_0^B. \quad (35)$$

From (34) and (35) we find that functions $\Psi_0^A(\mathbf{n}\cdot\mathbf{n}_A)$ and $\Psi_0^B(\mathbf{n}\cdot\mathbf{n}_B)$ in a polar coordinate system have the following forms:

$$\begin{aligned}\Psi_0^A(\mathbf{n}\cdot\mathbf{u}_A) &= g_A(\cos\Theta_A)\mathbf{\Theta}\cdot\mathbf{e}_\varphi^{\mathbf{A}},\\ \Psi_0^B(\mathbf{n}\cdot\mathbf{u}_B) &= g_B(\cos\Theta_B)\mathbf{\Theta}\cdot\mathbf{e}_\varphi^{\mathbf{B}},\end{aligned} \quad (36)$$

where $\cos\Theta_{A,B} = \mathbf{n}\cdot\mathbf{u}_{\mathbf{A,B}}$ and $\mathbf{e}_\varphi^{\mathbf{A,B}}$ is a unit vector parallel to $(1/\sin\Theta_{A,B})\ \partial\mathbf{u}_{\mathbf{A,B}}/\partial\varphi_{A,B}$ and functions g_A and g_B are determined by two equations:

$$\frac{1}{\sin\Theta_A}\frac{d}{d\Theta_A}\left(\sin\Theta_A\frac{dg_A}{d\Theta_A}\right) - \frac{g_A}{\sin^2\Theta_A} - \beta\frac{dV_0^A}{d\Theta_A}\frac{dg_A}{d\Theta_A} = -\beta\frac{dV_0^A}{d\Theta_A} \quad (37)$$

and

$$\frac{1}{\sin\Theta_B}\frac{d}{d\Theta_B}\left(\sin\Theta_B\frac{dg_B}{d\Theta_B}\right) - \frac{g_B}{\sin^2\Theta_B} - \beta\frac{dV_0^B}{d\Theta_B}\frac{dg_B}{d\Theta_B} = -\beta\frac{dV_0^B}{d\Theta_B}, \quad (38)$$

where V_0^A and V_0^B are defined in (21). From (36) we obtain also that both averages $\langle\Psi_0^A\rangle$ and $\langle\Psi_0^B\rangle$ are equal to zero. Finally Eq. (33) becomes

$$0 = \langle\mathcal{R}_A\omega_{\mathbf{A}}\Psi_0^A\rangle\frac{C_A}{D_A} + \langle\mathcal{R}_B\omega_{\mathbf{B}}\Psi_0^B\rangle\frac{C_B}{D_B}. \quad (39)$$

By substituting $C_A = kTd_A$ and $C_B = kTd_A$ and using relations (37) and (38) we can rewrite [2] the above equation in the form

$$0 = \mathbf{n}\times\left\{\left(\frac{d_A S_2^A}{D_A}f(p_A) + \frac{d_B S_2^B}{D_B}f(p_B)\right)kT\hat{\mathbf{A}}\cdot\mathbf{n} - \left(\frac{d_A\langle g_A\beta dV_0^A/d\Theta_A\rangle}{2D_A} + \frac{d_B\langle g_B\beta dV_0^B/d\Theta_B\rangle}{2D_B}\right)kT\hat{\mathbf{\Omega}}\cdot\mathbf{n}\right\}. \quad (40)$$

From (40) one finds that the formula for extinction angle χ reads as

$$\cos 2\chi = -\frac{\gamma_1}{\gamma_2} = \frac{1}{2}\frac{d_A D_B\langle g_A\beta dV_0^A/d\Theta_A\rangle + d_B D_A\langle g_B\beta dV_0^B/d\Theta_B\rangle}{d_A S_2^A f(p_A)D_B + d_B S_2^B f(p_B)D_A} \quad (41)$$

VI. THE LESLIE COEFFICIENTS

Comparing (23) with (11) and (40) with (12) we obtain

$$\begin{aligned}\alpha_1 &= -kT\left(\frac{d_A f(p_A)^2}{D_A}S_4^A + \frac{d_B f(p_B)^2}{D_B}S_4^B\right),\\ \alpha_2 &= -\frac{kT}{2}\left(\frac{d_A f(p_A)}{D_A}[S_2^A + \tfrac{1}{2}\langle g_A\beta dV_0^A/d\Theta_A\rangle/f(p_B)] + \frac{d_B f(p_B)}{D_B}[S_2^B + \tfrac{1}{2}\langle g_B\beta dV_0^B/d\Theta_B\rangle/f(p_B)]\right),\\ \alpha_3 &= -\frac{kT}{2}\left(\frac{d_A f(p_A)}{D_A}[S_2^A - \tfrac{1}{2}\langle g_A\beta dV_0^A/d\Theta_A\rangle/f(p_B)] + \frac{d_B f(p_B)}{D_B}[S_2^B - \tfrac{1}{2}\langle g_B\beta dV_0^B/d\Theta_B\rangle/f(p_B)]\right),\\ \alpha_4 &= \frac{kT}{35}\left(\frac{d_A f(p_A)^2}{D_A}(7 - 5S_2^A - 2S_4^A) + \frac{d_B f(p_B)^2}{D_B}(7 - 5S_2^B - 2S_4^B)\right),\end{aligned} \quad (42)$$

$$\alpha_5 = \frac{kT}{2}\left[\frac{d_A f(p_A)}{D_A}\left(\frac{f(p_A)}{7}(3S_2^A + 4S_4^A) + S_2^A\right) + \frac{d_B f(p_B)}{D_B}\left(\frac{f(p_B)}{7}(3S_2^B + 4S_4^B) + S_2^B\right)\right],$$

$$\alpha_6 = \frac{kT}{2}\left[\frac{d_A f(p_A)}{D_A}\left(\frac{f(p_A)}{7}(3S_2^A + 4S_4^A) - S_2^A\right) + \frac{d_B f(p_B)}{D_B}\left(\frac{f(p_B)}{7}(3S_2^B + 4S_4^B) - S_2^B\right)\right].$$

In particular, the rotational viscosity coefficient γ_1 is given by the following formula:

$$\gamma_1 = \alpha_3 - \alpha_2 = 2(d_A + d_B)\left(\frac{\langle g_A \beta d V_0^A / d\Theta_B\rangle}{D_A} x_A + \frac{\langle g_B \beta d V_0^B / d\Theta_B\rangle}{D_B} x_B\right), \tag{43}$$

where x_A and x_B denote the molar fractions of components. This relation is in agreement with known results [10], where the rule of averaging the rotational friction constants has been confirmed experimentally.

It is straightforward to see that formulas (42) obey the Parodi relation. In the limiting cases, when concentrations of components A or B tend to zero, we recover appropriate Doi formulas for the one-component system consisting of molecules A or B, respectively.

VII. CONCLUSION

On the basis of the Doi approach we have calculated the six Leslie viscosity coefficients, $\alpha_1 \cdots \alpha_6$, for binary mixtures of nematic liquid crystals. Obtained formulas fully recover the Doi expressions for one-component systems. Our results, however, are more general because we do not restrict ourselves to interaction potentials depending on the inner product $\mathbf{u}_1 \cdot \mathbf{u}_2$.

Our approach predicts that each of six viscosity coefficients, α_i, of the binary mixture is a sum of two Doi coefficients, α_i^A and α_i^B, characterizing the components A and B, respectively, weighted by the molar fractions. On the other hand, appropriate order parameters and rotational diffusion constants, appearing in α_i^A and α_i^B, are nontrivial functionals depending on the total features of the considered mixture. This rule of the arithmetic averaging has been confirmed in several experiments for the rotational viscosity coefficient γ_1. Therefore, the mean-field approximation, which we have used in these calculations, seems to be sufficient to stud the viscous properties of mixtures.

ACKNOWLEDGEMENT

This work was supported by the Polish Government Project No. KBN 2P30216704.

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