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Viscous properties of biaxial nematic liquid crystals: The method of calculation of the Leslie viscosity coefficients

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We present a microscopic approach to the theory of viscosity of biaxial nematic liquid crystals consistent with the existing 2-director continuum Leslie's theory and show the method of obtaining microscopic formulas for viscosity coefficients. The derived formulas are expressed in terms of order parameters, temperature, number density, and diffusion constants. Obtained viscosity coefficients satisfy the four Onsager-Parodi relations. Since no assumptions about diffusion constants are applied and a very general form of an interaction potential is used, presented results are quite general. The approximation concerns shapes of the molecules that are modeled by ellipsoids with three different principal axes. In the limiting case, when appropriate biaxial order parameters vanish and the system becomes uniaxial, we obtain the six Leslie viscosities involving, in general, two diffusion coefficients related to the rotational motion about short and long axes, respectively, and two ellipsoidal axis ratios. When the molecules possess symmetry axes, the formulas for the Leslie coefficients recover known results for uniaxial system. [S1063-651X(97)14202-7]

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I. INTRODUCTION

Since the discovery by Yu and Saupe [1] of the biaxial nematic liquid crystal, several macroscopic theories have been developed to describe properties of these interesting mesophases. Especially, the hydrodynamics of biaxial systems has been the subject of much interest. In fact, a number of continuum theories have been derived for biaxial nematic. The first formulation was given by Saupe [2], the subsequent by Kini [3], Govers and Vertogen [4], and Chauré [5]. The most complete derivation of the continuum theory has recently been given by Leslie *et al.* [6]. The two first theories mentioned [2,3] employ three orthonormal directors to describe the local anisotropy, whereas the two last approaches [5,6] introduce only two directors. However, as shown by Das and Schwarz [7], both the 3-director and the 2-director formulations of continuum theory are fully equivalent. This equivalence consists in that each viscosity coefficient in one model is expressible as a linear combination of the viscosity coefficients of the other model. In this paper we focus on the 2-director formulation and adopt the notation of Ref. [6].

An efficient microscopic approach to the dynamics of a nematic liquid crystal consisting of biaxial molecules is based on the rotational diffusion model, which assumes that the reorientation of an individual molecule is a stochastic Brownian motion in a certain potential of mean torque [8–12]. In such a treatment the system is determined by the time-dependent one-particle orientational distribution function governed by an appropriate kinetic equation. In general, while asymmetric molecules reorienting in an arbitrary mean potential are considered, the problem of finding the distribution function is a rather complex one and no closed analytical solution is available. On the other hand, Berggren and Zannoni [13] have recently solved the rotational diffusion equation for a biaxial system composed by asymmetric molecules.

However, whereas both the phenomenological and molecular descriptions seem to be well established, a relationship between them is not clear yet; to our knowledge, there is no appropriate microscopic theory that would allow one to express phenomenological quantities in terms of molecular parameters used on the microscopic level. Unfortunately, some attempts at the derivation of such a theory that have been made recently [7,14,15] are far from being satisfactory.

It should be also noted that analogous theories have been successfully developed for the uniaxial case. The appropriate phenomenological constitutive equations were proposed by Ericsen and Leslie [16,17]. On the other hand, many microscopic approaches [18–26] allow one to derive the constitutive equations from a molecular level and to express the viscosity coefficients in terms of the parameters characterizing the suspension. Note that a complete description of the microscopic origins of viscosity of nematic liquid crystals was presented by Kuzuu and Doi [19] and by Osipov and Terentjev [23]. Recently, Osipov *et al.* [27] developed also a consistent microscopic theory for describing viscosity of biaxial smectics C.

The purpose of this paper is therefore to relate both macroscopic and microscopic approaches and to present a method that allows us to express the phenomenological viscosity coefficients in terms of molecular parameters, such as order parameters, temperature, diffusion constants, number density, and some factors characterizing the molecular shape.

The paper is organized as follows. In Sec. II we summarize basic equations of the 2-director continuum theory of biaxial nematic liquid crystals. Section III presents a molecular approach to biaxial nematics and, as a main result, provides a system of three kinetic equations governing the one-particle distribution function. Sections IV and V present a method of obtaining the symmetric and the antisymmetric parts of the viscous stress tensor, respectively. Next, in Sec. VI, having obtained the complete viscous stress tensor, we calculate the sixteen Leslie viscosity coefficients. Finally, in Sec. VII, we discuss the derived formulas for the viscosity coefficients in the limit of uniaxial symmetry. Some com-

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ments on the methods presented are given in Sec. VIII.

II. THE BIAXIAL NEMATIC VISCOUS STRESS TENSOR

In this section we briefly summarize the most complete formulation of continuum theory for biaxial liquid crystals given by Leslie *et al.* in Ref. [6] and by Leslie in Ref. [28].

An incompressible, homogeneous biaxial nematic liquid crystal is under consideration. To describe the biaxiality we employ two orthogonal unit vectors $\underline{\boldsymbol{n}}$ and $\underline{\boldsymbol{m}}$. We introduce also two second-rank tensors, $\boldsymbol{A}$ and $\boldsymbol{\Omega}$, which correspond to the symmetric part and the antisymmetric part of the velocity gradient tensor $\partial_i v_j$, respectively:

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

Accordingly, the viscous stress tensor σ_{ij} is given by the following equation:

$$\begin{aligned}\sigma_{ij}={}&\alpha_1\underline{n}_k\underline{n}_pA_{kp}\underline{n}_i\underline{n}_j+\alpha_2N_i\underline{n}_j+\alpha_3N_j\underline{n}_i+\alpha_4A_{ij}\\&+\alpha_5A_{ik}\underline{n}_k\underline{n}_j+\alpha_6A_{jk}\underline{n}_k\underline{n}_i+\beta_1\underline{m}_k\underline{m}_pA_{kp}\underline{m}_i\underline{m}_j\\&+\beta_2M_i\underline{m}_j+\beta_3M_j\underline{m}_i+\beta_5A_{ik}\underline{m}_k\underline{m}_j+\beta_6A_{jk}\underline{m}_k\underline{m}_i\\&+N_p\underline{m}_p(\mu_1\underline{m}_i\underline{n}_j+\mu_2\underline{m}_j\underline{n}_i)+\underline{n}_kA_{kp}\underline{m}_p(\mu_3\underline{m}_i\underline{n}_j\\&+\mu_4\underline{m}_j\underline{n}_i)+\mu_5\underline{m}_k\underline{m}_pA_{kp}\underline{n}_i\underline{n}_j,\end{aligned} \tag{2.1}$$

where

$$\boldsymbol{N}=\dot{\underline{\boldsymbol{n}}}-\boldsymbol{\Omega}\cdot\underline{\boldsymbol{n}}, \quad \boldsymbol{M}=\dot{\underline{\boldsymbol{m}}}-\boldsymbol{\Omega}\cdot\underline{\boldsymbol{m}}. \tag{2.2}$$

The vectors $\boldsymbol{N}$ and $\boldsymbol{M}$ represent the rate of change of the directors with respect to the moving fluid. The coefficients $\alpha_1,\ldots,\alpha_6$, $\beta_1,\ldots,\beta_6$, and $\mu_1,\ldots,\mu_5$ will be referred to as the Leslie viscosity coefficients. They are linked by the following four Onsager-Parodi relations [29,6]:

$$\begin{aligned}&\alpha_3+\alpha_2=\alpha_6-\alpha_5,\\&\beta_3+\beta_2=\beta_6-\beta_5,\\&\mu_1+\mu_2=\mu_4-\mu_3,\\&\mu_5=0.\end{aligned} \tag{2.3}$$

Therefore, to describe the system completely, one has to know twelve linearly independent viscosity coefficients.

The equation representing the balance of angular momentum can be written [28] in the following form of two vector equations:

$$\tilde{g}_i^n=-(\gamma_1N_i+\gamma_2A_{ij}\underline{n}_j+\gamma_3N_j\underline{m}_j\underline{m}_i+\gamma_4\underline{n}_jA_{jk}\underline{m}_k\underline{m}_i), \tag{2.4}$$

$$\tilde{g}_i^m=-(\lambda_1M_i+\lambda_2A_{ij}\underline{m}_j), \tag{2.5}$$

where the vectors $\tilde{g}_i^n$ and $\tilde{g}_i^m$ are defined as follows:

$$\tilde{g}_i^n=\gamma\underline{n}_i+\kappa\underline{m}_i, \quad \tilde{g}_i^m=\tau\underline{m}_i+\kappa\underline{n}_i, \tag{2.6}$$

with γ, κ, and τ being certain constants. The coefficients that appear in Eqs. (2.4) and (2.5) are related to the Leslie coefficients by

$$\gamma_1=\alpha_3-\alpha_2, \quad \gamma_2=\alpha_6-\alpha_5, \quad \gamma_3=\mu_2-\mu_1,$$

$$\gamma_4=\mu_4-\mu_3, \quad \lambda_1=\beta_3-\beta_2, \quad \lambda_2=\beta_6-\beta_5.$$

For some reasons, however, we will use the balance equations of angular momentum Eq. (2.6) rewritten in a fully equivalent form of a system of the following three scalar equations:

$$(\gamma_1N_i+\gamma_2A_{ij}\underline{n}_j)\underline{l}_i=0, \tag{2.7}$$

$$(\lambda_1M_i+\lambda_2A_{ij}\underline{m}_j)\underline{l}_i=0, \tag{2.8}$$

$$[(\gamma_1+\gamma_3+\lambda_1)N_i+(\gamma_2+\gamma_4-\lambda_2)A_{ij}\underline{n}_j]\underline{m}_j=0, \tag{2.9}$$

where $\underline{\boldsymbol{l}}=\underline{\boldsymbol{m}}\times\underline{\boldsymbol{n}}$.

III. KINETIC EQUATIONS FOR A BIAXIAL SYSTEM

We consider a spatially homogeneous system consisting of biaxial molecules affected by a low velocity gradient field. The orientation of each molecule is described by the rotation $\boldsymbol{R}$, which transforms the set of laboratory coordinates into the set of coordinates fixed in this molecule. Such rotation can be represented by the collection of the three Euler angles [30], $\boldsymbol{R}\equiv(\varphi,\theta,\psi)$. The elements of the first set of coordinates, i.e., three mutually perpendicular versors $\underline{\boldsymbol{l}}$, $\underline{\boldsymbol{m}}$, and $\underline{\boldsymbol{n}}$, describe the biaxiality of the system and are identical to those just introduced in the previous section. The second set of coordinates, containing the versors $\boldsymbol{l}$, $\boldsymbol{m}$, and $\boldsymbol{n}$, is chosen in accordance with the molecular symmetry, in such a way that the versor $\boldsymbol{n}$ coincides with the long axis $\boldsymbol{c}$, versor $\boldsymbol{m}$ with the short axis $\boldsymbol{b}$, and versor $\boldsymbol{l}$ with the short axis $\boldsymbol{a}$. Moreover, to focus our attention, we assume that $c>b>a$, where where c, b, and a are the lengths of the appropriate principal axes.

The probability that at time t the molecule is rotated away from the laboratory coordinates through a certain rotation $\boldsymbol{R}$ is given by the one particle orientational distribution function $F(\boldsymbol{R},t)$. In order to obtain the kinetic equation governing the time evolution of $F(\boldsymbol{R},t)$ we assume that the rotational motion of a selected molecule may be treated as Brownian motion in a certain external potential U, which corresponds to an effective interaction with surrounding molecules. Such an approach is closely related to the mean-field approximation, which is assumed to be sufficient in the problem we consider. Moreover, we assume that the Brownian motion of each of the three symmetry axes proceeds independently. Therefore we are guaranteed that in the appropriate molecular frame of reference the diffusion tensor, which will be discussed later, is diagonal.

Within the framework of the mean-field approach, the potential U is given by the following functional of the probability function $F(\boldsymbol{R},t)$:

$$U=U[F,\mathbf{R},t]=d\int K(\mathbf{R},\mathbf{R}')F(\mathbf{R}',t)\mathbf{d}R', \qquad (3.1)$$

where we have used an abbreviation: $\mathbf{d}R\equiv\sin\theta d\theta d\varphi d\psi$ and d denotes the number density of molecules. The kernel $K(\mathbf{R},\mathbf{R}')$ corresponds to an interaction potential between a pair of molecules. In this paper, however, we do not have to know an explicit form of $K(\mathbf{R},\mathbf{R}')$. It can be a quite general function of $\mathbf{R}$ and $\mathbf{R}'$ allowed by the symmetry requirements. It should be also noted that the functional $U[F]$ given by Eq. (3.1) is a linear one. We will make use of this fact in further calculations.

The appropriate Fokker-Planck type equation determining the time evolution of the one-particle orientational distribution function $F(\mathbf{R},t)$ reads

$$\frac{\partial F}{\partial t}=L_iD_{ij}\left[L_jF-\frac{F}{kT}L_jU[F]\right]-L_i(\omega_iF), \qquad (3.2)$$

where T is the absolute temperature, k is the Boltzmann constant, and $U[F]$ is the above-mentioned mean-field potential; L_i are components of the angular momentum operator, which satisfy the usual commutation relations

$$[L_i,L_j]=i\epsilon_{ijk}L_k,$$

where ϵ_{ijk} is the completely antisymmetric unit tensor.

The last term in Eq. (3.2) is due to the velocity gradient, which rotates each molecule with a certain average angular velocity $\boldsymbol{\omega}$. In order to determine this angular velocity we model the biaxial molecule as an ellipsoid with three different principal axes $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ and make use of the Jefferey [31] solution for the motion of a single ellipsoid in a homogeneous shear flow. For the ellipsoid with a long principal axis $\mathbf{c}$ parallel to versor $\mathbf{n}$ and with short axes $\mathbf{b}$ and $\mathbf{a}$ parallel, respectively, to $\mathbf{m}$ and $\mathbf{l}$ an appropriate formula for the angular velocity is given by

$$\boldsymbol{\omega}=-\mathbf{l}\left[\mathbf{m}\cdot\left(\frac{b^2-c^2}{b^2+c^2}\mathbf{A}-\boldsymbol{\Omega}\right)\cdot\mathbf{n}\right]+\mathbf{m}\left[l\cdot\left(\frac{c^2-a^2}{c^2+a^2}\mathbf{A}-\boldsymbol{\Omega}\right)\cdot\mathbf{n}\right]+\mathbf{n}\left[m\cdot\left(\frac{a^2-b^2}{a^2+b^2}\mathbf{A}-\boldsymbol{\Omega}\right)\cdot\mathbf{l}\right]. \qquad (3.3)$$

Finally, in the Fokker-Planck equation (3.2) D_{ij} stands for the rotational diffusion tensor, whose elements are given by

$$D_{ij}=D_ll_il_j+D_mm_im_j+D_nn_in_j, \qquad (3.4)$$

where the constants D_l, D_m, and D_n are, respectively, the rotational diffusion coefficients around the $\mathbf{l}$, $\mathbf{m}$, and $\mathbf{n}$ principal axes of an ellipsoid in the molecular frame of reference (in which D_{ij} is diagonal). As seen, the rotational diffusion matrix is a symmetric one. Note also that in the case of isotropic diffusion, i.e., when $D_l=D_m=D_n=D$, tensor D_{ij} can be written, using the identity

$$l_il_j+m_im_j+n_in_j=\delta_{ij}, \qquad (3.5)$$

simply as $D_{ij}=D\delta_{ij}$, where δ_{ij} denotes the Kronecker symbol. Note that a similar form of the kinetic equation was also used by several authors [8,13,15].

The Fokker-Planck equation (3.2) may be written in the equivalent form of the continuity equation

$$\frac{\partial F}{\partial t}=L_iJ_i, \qquad (3.6)$$

where J_i are components of the probability current $\mathbf{J}$ and L_iJ_i should be understood as its generalized angular divergence. The three components of the probability current $\mathbf{J}$ are defined as follows:

$$J_i=D_{ij}L_jF+\frac{F}{kT}D_{ij}L_jU[F]-F\omega_i. \qquad (3.7)$$

If we project the vector $\mathbf{J}$ onto the versors $\mathbf{l}$, $\mathbf{m}$, and $\mathbf{n}$ successively (i.e., if we find components of $\mathbf{J}$ in the molecular frame of reference), then make use of Eq. (3.4) defining the diffusion tensor, as a result we obtain the following system of three scalar equations:

$$l_iJ_i=D_ll_iL_iF-\frac{D_l}{kT}Fl_iL_iU[F]-Fl_i\omega_i, \qquad (3.8)$$

$$m_iJ_i=D_mm_iL_iF-\frac{D_m}{kT}Fm_iL_iU[F]-Fm_i\omega_i, \qquad (3.9)$$

$$n_iJ_i=D_nn_iL_iF-\frac{D_n}{kT}Fn_iL_iU[F]-Fn_i\omega_i. \qquad (3.10)$$

In further considerations the above three constitutive equations, derived from the definition (3.7), will be called simply the probability current (PC) equations.

In general, there is no reason to assume that in a stationary state the probability current is a constant vector. Thus we have to consider components of $\mathbf{J}$ being functions depending on a collection of Euler angles, i.e., $J_i=J_i(\mathbf{R})$. However, the number of all J_i functions we should take into account is limited by the symmetry of the biaxial phase, which yields the constraint that application of the D_{2h} group operations should leave J_i unchanged. The second restriction is obviously that the condition $L_iJ_i(\mathbf{R})=0$ holds. Moreover, in equilibrium, i.e., when the velocity gradient is not present, all components of the probability current vanish. We show that it follows immediately from the fact that both the Hammerstein-type equation for the one-particle distribution function, derived in the framework of a functional approach, and the kinetic Fokker-Planck equation must be consistent and obeyed by the same equilibrium distribution function F_0.

Let $\mathcal{F}=U_{\text{int}}-TS$ denote the Helmholtz free energy of the system we consider. Here U_{int} and S stand for the internal energy and the entropy of the system, respectively, and T is the absolute temperature. At the level of the second virial coefficient $\mathcal{F}$ is the following functional depending on the one particle orientational distribution function $F(\mathbf{R})$ [32–34]:

$$\mathcal{F}[F]=dkT\int F(\boldsymbol{R})\ln[F(\boldsymbol{R})]\boldsymbol{dR} - \frac{d^2}{2}\int\int F(\boldsymbol{R})F(\boldsymbol{R}')K(\boldsymbol{R},\boldsymbol{R}')\boldsymbol{dRdR}'. \tag{3.11}$$

To obtain the condition for equilibrium we require that the functional $\mathcal{F}$ must be a minimum with respect to an arbitrary variation of F_0, i.e., $\delta\mathcal{F}[F]/\delta F=0$ for $F=F_0$. This leads to

$$\ln(F_0)-\frac{1}{kT}U[F_0]=\mu, \tag{3.12}$$

where μ denotes a chemical potential and $U[F_0]$ is the mean-field potential defined in Eq. (3.1). Equation (3.12) is just the above-mentioned self-consistent Hammerstein equation governing the equilibrium solution F_0.

As a result of the action of the $D_{ij}L_j$ operator upon Eq. (3.12) we obtain

$$D_{ij}\left[L_jF_0-\frac{F_0}{kT}L_jU[F_0]\right]=0.$$

The left-hand side of the above expression is, according to Eq. (3.7), the ith component of the probability current. Thus, in equilibrium the vector $\boldsymbol{J}(\boldsymbol{R})$ vanishes.

If the system is subjected to the shear flow, the probability current $\boldsymbol{J}(\boldsymbol{R})$ appears and the equilibrium distribution function F_0 changes to the stationary solution $F=F_0+\delta F$. We can write both the perturbation δF and the probability current in terms of the Wigner matrices $D^l_{\alpha\beta}(\boldsymbol{R})$ as

$$J_i(\boldsymbol{R})=\sum_l\sum_{\alpha\beta}D^l_{\alpha\beta}(\boldsymbol{R})j_i^{l,\alpha\beta}, \tag{3.13}$$

$$\delta F(\boldsymbol{R})=\sum_l\sum_{\alpha\beta}D^l_{\alpha\beta}(\boldsymbol{R})f^{l,\alpha\beta}, \tag{3.14}$$

where $j_i^{l,\alpha\beta}$ and $f^{l,\alpha\beta}$ are certain expansion coefficients. Note that the summation must be taken over both odd and even l, since the velocity gradient affects the directors $\underline{\boldsymbol{l}}$, $\underline{\boldsymbol{m}}$, and $\underline{\boldsymbol{n}}$.

It should be emphasized that our goal is not to find either the stationary solution $F(\boldsymbol{R})$ or $\boldsymbol{J}(\boldsymbol{R})$; the actual object of our considerations is the PC equations. We analyze these equations only for the purpose of coming up with information about the viscous stress tensor and properties of a nonequilibrium solution are not of our interest here.

In general, there are two separate effects caused by the shear: First, it makes the directors $\underline{\boldsymbol{l}}$, $\underline{\boldsymbol{m}}$, and $\underline{\boldsymbol{n}}$ rotate away from their equilibrium positions. Second, it changes values of the scalar order parameters. In this paper, however, we take into consideration flow-induced disturbances being pure rotations of the directors only. The shear flow is treated as a small perturbation, which removes degeneration of the equilibrium state. The system is thus rotated about a small angle $\boldsymbol{\delta R}$ whereas all scalar order parameters remain unchanged. Note that the viscosity coefficients are expressed in terms of quantities that are averages taken over the equilibrium distribution function F_0; the question of how the velocity gradient affects scalar order parameters characterizing the biaxial phase is not of our interest. The task we are dealing with has in fact nothing in common with nonequilibrium problem.

Since the angle $\boldsymbol{\delta R}$ is a small quantity being of order of perturbation, we can apply the Taylor expansion and retain only terms linear in $\boldsymbol{\delta R}$. We have

$$\delta F(\boldsymbol{R})=-\boldsymbol{\delta R}\cdot\boldsymbol{L}F_0(\boldsymbol{R}). \tag{3.15}$$

In Appendix B we show also that the fact that we confine ourselves to very small perturbations yields considerable limitations for the family of the currents $\boldsymbol{J}$ we have to take into account.

In the following section we use the obtained PC equations (3.8)–(3.10) in order to derive the symmetric part of the viscous stress tensor and express it in terms of suspension parameters. Next, in Sec. V we show the method that allows us to recover the phenomenological balance equations for angular momentum (2.7)–(2.9) on the basis of the PC equation set mentioned, and, thereby, obtain the antisymmetric part of the stress tensor.

IV. THE SYMMETRIC PART OF THE MICROSCOPIC STRESS TENSOR

In this section we show a method that allows us to derive the symmetric part of the viscous stress tensor. We adopt the method introduced by Doi [18] and Kuzuu and Doi [19] in the case of uniaxial nematics and extend it to the biaxial case.

The method we use is based, in general, on analyzing the change in the free energy caused by the shear flow. It should be emphasized that this analysis cannot provide information concerning the antisymmetric part of the stress at all because the system is uniform, no external field is present, and all averages are taken over the equilibrium distribution function. Thus, in this section we come up with information about the symmetric part of the stress tensor only. The antisymmetric part is derived separately in Sec. V.

We consider a system consisting of biaxial molecules undergoing the influence of a small velocity gradient field. This field causes each molecule to move along a periodic Jefferey orbit with the average angular velocity $\boldsymbol{\omega}$ given by Eq. (3.3). Therefore, in the infinitesimal time δt orientation of the individual molecule is changed by a small angle $\boldsymbol{\delta\Theta}$:

$$\delta\Theta_i=\omega_i\delta t=-\left[-\frac{c^2}{b^2+c^2}l_im_pn_q+\frac{a^2}{a^2+c^2}m_il_pn_q+\frac{b^2}{a^2+b^2}n_im_pl_q\right]\epsilon_{qp}+\left[-\frac{b^2}{b^2+c^2}l_im_pn_q+\frac{c^2}{a^2+c^2}m_il_pn_q+\frac{a^2}{a^2+b^2}n_im_pl_q\right]\epsilon_{pq}, \tag{4.1}$$

where $\epsilon_{pq}=\partial_pv_q\delta t$ can be regarded as a hypothetical small deformation tensor. [Of course, we can describe the orientation of a selected molecule using the Eulerian angles or equivalently the director triad $(\boldsymbol{l},\boldsymbol{m},\boldsymbol{n})$. However, a natural choice while dealing with Cartesian tensors is using the latter. Therefore the angle $\boldsymbol{\delta\Theta}$, which appears in Eq. (4.1), is an ordinary three-dimensional Cartesian vector.] Accordingly, the distribution function $F(R,t)$ is changed from F_0 to F':

$$F' = F_0 + \delta F = F_0 - \boldsymbol{L}(\boldsymbol{\delta\Theta} F_0), \tag{4.2}$$

where $\boldsymbol{L}$ is the angular momentum operator introduced in the previous section.

The change $\delta\mathcal{F} = \mathcal{F}[F'] - \mathcal{F}[F_0]$ in the free energy due to the small variation δF of the distribution function, according to Eq. (3.11), has the form

$$\delta\mathcal{F} = dkT \int \delta F(\boldsymbol{R}) \boldsymbol{dR} + dkT \int \delta F(\boldsymbol{R}) \ln[F_0(\boldsymbol{R})] \boldsymbol{dR} - d \int U[F_0, \boldsymbol{R}] \delta F(\boldsymbol{R}) \boldsymbol{dR}. \tag{4.3}$$

Using Eq. (4.2) and applying the rule of integration by parts we can rewrite the above equation in a more convenient form as

$$-\delta\mathcal{F}/dkT = \langle \boldsymbol{L\delta\Theta} \rangle + \langle \boldsymbol{\delta\Theta L} U_0 \rangle, \tag{4.4}$$

where the averages are taken over the equilibrium distribution function and $U_0 \equiv U[F_0]$ is the appropriate equilibrium mean-field potential.

According to the elasticy theory, the symmetric part of the viscous stress tensor $\boldsymbol{\sigma}^{\mathrm{sym}} \equiv (\boldsymbol{\sigma} + \boldsymbol{\sigma}^{\dagger})/2$ is connected with $\delta\mathcal{F}$ by the following relation:

$$\delta\mathcal{F} = \sigma^{\mathrm{sym}}_{\alpha\beta} \epsilon^{\dagger}_{\alpha\beta}. \tag{4.5}$$

It should be emphasized here that the analysis of the free energy functional we use in this section always produces the symmetric part of the stress tensor, provided no external field is present and the system is uniform.

Combining Eqs. (4.4) and (4.5) and using Eq. (3.3), we obtain an expression for the microscopic stress tensor $\sigma^{\mathrm{sym}}_{pq}$:

$$\begin{aligned}\sigma^{\mathrm{sym}}_{pq} = {} & -dkT[\langle n_p n_q \rangle (f_m + f_l) - \langle m_p m_q \rangle (f_l + f_n) \\ & + \langle l_p l_q \rangle (f_n - f_m)] + \frac{d f_l}{2} \langle (m_p n_q + m_q n_p) l_i L_i U_0 \rangle \\ & - \frac{d}{2} \langle (m_p n_q - m_q n_p) l_i L_i U_0 \rangle \\ & - \frac{d f_m}{2} \langle (l_p n_q + l_q n_p) m_i L_i U_0 \rangle \\ & + \frac{d}{2} \langle (l_p n_q - l_q n_p) m_i L_i U_0 \rangle \\ & - \frac{d f_n}{2} \langle (m_p l_q + m_q l_p) n_i L_i U_0 \rangle \\ & + \frac{d}{2} \langle (m_p l_q - m_q l_p) n_i L_i U_0 \rangle, \end{aligned} \tag{4.6}$$

where

$$f_l = \frac{b^2 - c^2}{b^2 + c^2}, \quad f_m = \frac{a^2 - c^2}{c^2 + a^2}, \quad f_n = \frac{a^2 - b^2}{a^2 + b^2}. \tag{4.7}$$

Before proceeding to further calculations we notice that the above equation for the viscous stress tensor together with the kinetic Fokker-Planck equation (3.2) governing the distribution function $F(\boldsymbol{R}, t)$ should be regarded as rheological constitutive equations for the biaxial system we consider.

It is convenient to rewrite the expression (4.6) in the evidently symmetric form making use of the obvious fact that $\sigma^{\mathrm{sym}}_{pq} = (\sigma^{\mathrm{sym}}_{pq} + \sigma^{\mathrm{sym}}_{qp})/2$,

$$\begin{aligned}\sigma^{\mathrm{sym}}_{pq} = {} & -dkT[\langle n_p n_q \rangle (f_m + f_l) - \langle m_p m_q \rangle (f_l + f_n) \\ & + \langle l_p l_q \rangle (f_n - f_m)] + \frac{d}{2} [f_l \langle (m_p n_q + m_q n_p) l_i L_i U_0 \rangle \\ & - f_m \langle (l_p n_q + l_q n_p) m_i L_i U_0 \rangle \\ & - f_n \langle (m_p l_q + m_q l_p) n_i L_i U_0 \rangle]. \end{aligned} \tag{4.8}$$

One can also easily verify (see the Appendix A for details) that the antisymmetric part of the expression (4.6),

$$\frac{1}{2}(\sigma^{\mathrm{sym}}_{pq} - \sigma^{\mathrm{sym}}_{qp}) = -\frac{d}{2} \epsilon_{pqs} \langle l_s l_i L_i U_0 + m_s m_i L_i U_0 + n_s n_i L_i U_0 \rangle, \tag{4.9}$$

is in fact equal to zero.

It should be also noticed that if the system becomes uniaxial the formula (4.6) recovers the appropriate expression for the stress tensor from the paper by Kuzuu and Doi [19]. Indeed, assuming that $U_0 = U_0(\underline{\boldsymbol{n}} \cdot \boldsymbol{n})$ and $a = b$ we straightforwardly obtain

$$\boldsymbol{\sigma}^{\mathrm{sym}} = \frac{p^2 - 1}{p^2 + 1} \left[3dkT \left\langle \boldsymbol{nn} - \frac{1}{3} \mathbf{1} \right\rangle - d \langle \boldsymbol{n}(\boldsymbol{n} \times \mathcal{R} U_0) \rangle \right],$$

where $\mathcal{R} = \boldsymbol{n} \times \partial/\partial\boldsymbol{n}$, $p = c/a$, and $\mathbf{1}$ is the unit tensor. (To avoid a confusion note that the expression derived by Kuzuu and Doi contained also additional terms due to a fictitious magnetic field, which is not necessary in the method we propose.)

The symmetric part $\boldsymbol{\sigma}^{\mathrm{sym}}$ can be determined exactly without solving the PC equations. We make use of these equations only for the purpose of eliminating from Eq. (4.8) all terms involving the averages of $L_i U_0$. We evaluate $\langle (m_p n_q + m_q n_p) l_i L_i U_0 \rangle$, $\langle (l_p n_q + l_q n_p) m_i L_i U_0 \rangle$, and $\langle (m_p l_q + m_q l_p) n_i L_i U_0 \rangle$ in the following way.

Multiplying the PC equations by $m_p n_q$, $l_p n_q$, and $m_p l_q$, respectively, then substituting Eq. (3.3) for the angular velocity, and carrying out integration over $\boldsymbol{dR}$, we obtain, using the rule of integration by parts,

$$\begin{aligned}\langle (m_p n_q + m_q n_p) l_i L_i U_0 \rangle = {} & -\frac{1}{D_l} \int (m_p n_q + m_q n_p) l_i J_i(\boldsymbol{R}) \boldsymbol{dR} \\ & + 2kT \left[\langle n_p n_q \rangle - \langle m_p m_q \rangle + \frac{f_l}{2D_l} \langle (m_p n_q + m_q n_p) m_t n_s A_{ts} \rangle - \frac{1}{2D_l} \langle (m_p n_q + m_q n_p) m_t n_s \Omega_{ts} \rangle \right], \end{aligned}$$

$$\langle (l_p n_q + l_q n_p) m_i L_i U_0 \rangle = -\frac{1}{D_m}\int (n_p l_q + n_q l_p) m_i J_i(\boldsymbol{R}) \boldsymbol{dR}$$
$$+2kT\left[\langle l_p l_q\rangle - \langle n_p n_q\rangle - \frac{f_m}{2D_m}\langle (l_p n_q + l_q n_p) l_t n_s A_{ts}\rangle + \frac{1}{2D_m}\langle (l_p n_q + l_q n_p) l_t n_s \Omega_{ts}\rangle\right],$$

$$\langle (m_p l_q + m_q l_p) n_i L_i U_0 \rangle = -\frac{1}{D_n}\int (l_p m_q + l_q m_p) n_i J_i(\boldsymbol{R}) \boldsymbol{dR}$$
$$\times 2kT\left[\langle m_p m_q\rangle - \langle l_p l_q\rangle - \frac{f_n}{2D_n}\langle (m_p l_q + m_q l_p) m_t l_s A_{ts}\rangle + \frac{1}{2D_n}\langle (m_p l_q + m_q l_p) m_t l_s \Omega_{ts}\rangle\right].$$

We show in Appendix B that the three integrals involving the probability current, which appear in the above formulas, vanish provided we use $\boldsymbol{J}(\boldsymbol{R})$ given by Eq. (B1), which is linear in perturbation.

Making use of the constraint (3.5) to eliminate the versor $\boldsymbol{l}$ from the above expressions and inserting them into Eq. (4.8) we get

$$2\frac{\sigma_{ij}^{\rm sym}}{dkT} = -2\frac{f_m^2}{D_m}\langle n_i n_j n_k n_p\rangle A_{kp} - 2\frac{f_n^2}{D_n}\langle m_i m_j m_k m_p\rangle A_{kp} - \left(\frac{f_m^2}{D_m} + \frac{f_n^2}{D_n} - \frac{f_l^2}{D_l}\right)\langle n_i m_j n_k m_p A_{kp} + n_j m_i n_k m_p A_{kp}\rangle$$
$$+\frac{f_m^2}{D_m}\langle n_i n_k A_{jk} + n_j n_k A_{ik}\rangle + \frac{f_n^2}{D_n}\langle m_i m_k A_{jk} + m_j m_k A_{ik}\rangle + \frac{f_m}{D_m}\langle n_i n_k \Omega_{kj} + n_j n_k \Omega_{ki}\rangle + \frac{f_n}{D_n}\langle m_i m_k \Omega_{kj} + m_j m_k \Omega_{ki}\rangle$$
$$+\left(\frac{f_l}{D_l} - \frac{f_m}{D_m} - \frac{f_n}{D_n}\right)\langle n_i n_k m_j m_p \Omega_{kp} + m_i n_k n_j m_p \Omega_{kp}\rangle. \quad (4.10)$$

Therefore, to obtain the symmetric part of the viscous stress tensor we have to calculate equilibrium averages of fourth- and second-rank tensors being products of two unit vectors, i.e., $\boldsymbol{m}$ and $\boldsymbol{n}$. To find these averages we will make use of the following decoupling approximation:

$$\langle a_i b_j a_k A_{kp} b_p\rangle \cong \langle a_i b_j\rangle \langle a_k A_{kp} b_p\rangle, \quad (4.11)$$

$$\langle a_i b_j a_k \Omega_{kp} b_p\rangle \cong \langle a_i b_j\rangle \langle a_k \Omega_{kp} b_p\rangle, \quad (4.12)$$

where the symbols a_i and b_i stand for components of the versors $\boldsymbol{m}$ and $\boldsymbol{n}$, i.e., $a_i = m_i, n_i$ and $b_i = m_i, n_i$. The formulas (4.11) and (4.12) allow for expressing all averages of fourth-range tensors, which appear in Eq. (4.10), in terms of $\langle m_i m_j\rangle$, $\langle n_i n_j\rangle$, and $\langle n_i m_j + n_j m_i\rangle$ only.

The decoupling procedure we use in this paper is a natural extension to the biaxial case of the approximation of the form $\langle n_i n_j n_k n_p\rangle \cong \langle n_i n_j\rangle\langle n_k n_p\rangle$, which was used by Doi [18] and Marrucci [20] in the case of uniaxial nematic. A detailed justification of such an approximation is given in Ref. [18]. In general, such a decoupling procedure is rather rough and may produce errors being of the order of magnitude. However, importantly, it becomes correct in the limit of strong ordering. Therefore, the use of this decoupling procedure in calculations seems to be reasonable, especially if we deal with a deep biaxial phase. It also should be noted here that the Miesowicz viscosities obtained by Marrucci in the framework of the discussed decoupling approximation were in agreement with the experimental data. Moreover, he predicted, in principle, a correct dependence of the Leslie viscosity coefficients on the nematic order parameter. We can thus expect that applying Eqs. (4.11) and (4.12) in the case of biaxial nematic is reasonable too.

We proceed now to the calculation of the averages $\langle n_i n_j\rangle$ and $\langle m_i m_j\rangle$. For this purpose we first introduce two symmetric traceless second-rank tensors $S_{ij} = \langle n_i n_j - \delta_{ij}/3\rangle$ and $B_{ij} = \langle m_i m_j - l_i l_j\rangle$ describing a degree of order of the biaxial nematic liquid crystal we are dealing with. The first tensor is related to the uniaxial alignment, the second one describes the biaxial alignment (cf. Refs. [35,36]). Using the identity (3.5) we may obviously write tensor B_{ij} in terms of $\boldsymbol{n}$ and $\boldsymbol{m}$ only as $\langle 2m_i m_j + n_i n_j - \delta_{ij}\rangle$. It can be easily proved that the versors $\underline{\boldsymbol{m}}$ and $\underline{\boldsymbol{n}}$ are a common set of eigenvectors of the tensors S_{ij} and B_{ij}. Furthermore, we have the following relations, which allow us to relate both tensors to macroscopic quantities:

$$\langle \boldsymbol{nn} - \boldsymbol{1}/3\rangle = \langle F_{00}^2\rangle(\underline{\boldsymbol{n}}\,\underline{\boldsymbol{n}} - \boldsymbol{1}/3) + \frac{\sqrt{3}}{3}\langle F_{20}^2\rangle(2\underline{\boldsymbol{m}}\,\underline{\boldsymbol{m}} + \underline{\boldsymbol{n}}\,\underline{\boldsymbol{n}} - \boldsymbol{1}), \quad (4.13)$$

$$\langle 2\boldsymbol{mm} + \boldsymbol{nn} - \boldsymbol{1}\rangle = -\sqrt{3}\langle F_{02}^2\rangle(\underline{\boldsymbol{n}}\,\underline{\boldsymbol{n}} - \boldsymbol{1}/3) + \langle F_{22}^2\rangle \times (2\underline{\boldsymbol{m}}\,\underline{\boldsymbol{m}} + \underline{\boldsymbol{n}}\,\underline{\boldsymbol{n}} - \boldsymbol{1}), \quad (4.14)$$

where the functions $F_{ij}^l = F_{ij}^l(\boldsymbol{R})$ are the appropriate scalar invariants generating the solution space Γ of the D_{2h} symmetry group [34,37] and are described in detail in Appendix C. The above results follow immediately from the definition of the averaging we use: $\langle a_i b_j\rangle = \int a_i(\boldsymbol{R}) b_j(\boldsymbol{R}) F_0(\boldsymbol{R}) \boldsymbol{dR}$. Note also that both averages calculated, S_{ij} and B_{ij}, are linear combinations of two order matrices $(n_i n_j - \delta_{ij}/3)$ and $(2m_i m_j + n_i n_j - \delta_{ij})$ only.

From Eqs. (4.13) and (4.14) we obtain

$$\langle \boldsymbol{nn}\rangle = S\underline{\boldsymbol{n}}\,\underline{\boldsymbol{n}} + B_1\underline{\boldsymbol{m}}\,\underline{\boldsymbol{m}} + \tfrac{1}{3}(1-S+B_1)\mathbf{1}, \tag{4.15}$$

$$\langle \boldsymbol{mm}\rangle = S_1\underline{\boldsymbol{n}}\,\underline{\boldsymbol{n}} + B\underline{\boldsymbol{m}}\,\underline{\boldsymbol{m}} + \tfrac{1}{3}(1-S_1-B-B_1)\mathbf{1}, \tag{4.16}$$

where

$$S = \langle F_{00}^2\rangle + \sqrt{3}\langle F_{20}^2\rangle/3, \tag{4.17a}$$

$$B = \sqrt{3}\langle F_{20}^2\rangle/3 + \langle F_{22}^2\rangle, \tag{4.17b}$$

$$2S_1 = -\sqrt{3}\langle F_{02}^2\rangle + \langle F_{22}^2\rangle - \sqrt{3}\langle F_{20}^2\rangle/3 - \langle F_{00}^2\rangle, \tag{4.17c}$$

$$B_1 = \langle F_{22}^2\rangle + \sqrt{3}\langle F_{20}^2\rangle/3. \tag{4.17d}$$

Applying the decoupling procedure given by Eqs. (4.11) and (4.12) to the formula (4.10), then making use of Eqs. (4.15) and (4.16) we arrive at the following expression for the symmetric part of the viscous stress tensor:

$$\begin{aligned}2\boldsymbol{\sigma}^{\mathrm{sym}}/dkT = {} & -2\left(\frac{f_m^2}{D_m}S^2+\frac{f_n^2}{D_n}S_1^2\right)\underline{\boldsymbol{n}}\,\underline{\boldsymbol{n}}(\underline{\boldsymbol{n}}\,\underline{\boldsymbol{n}}\boldsymbol{:}\boldsymbol{A}) - 2\left(\frac{f_m^2}{D_m}B_1^2+\frac{f_n^2}{D_n}B^2\right)\underline{\boldsymbol{m}}\,\underline{\boldsymbol{m}}(\underline{\boldsymbol{m}}\,\underline{\boldsymbol{m}}\boldsymbol{:}\boldsymbol{A}) + \left(\frac{f_m^2}{D_m}S+\frac{f_n^2}{D_n}S_1\right)(\underline{\boldsymbol{n}}\,\underline{\boldsymbol{n}}\cdot\boldsymbol{A}+\boldsymbol{A}\cdot\underline{\boldsymbol{n}}\,\underline{\boldsymbol{n}}) \\ & + \left(\frac{f_m^2}{D_m}B_1+\frac{f_n^2}{D_n}B\right)(\underline{\boldsymbol{m}}\,\underline{\boldsymbol{m}}\cdot\boldsymbol{A}+\boldsymbol{A}\cdot\underline{\boldsymbol{m}}\,\underline{\boldsymbol{m}}) - 2\left(\frac{f_m^2}{D_m}SB_1+\frac{f_n^2}{D_n}BS_1\right)[\underline{\boldsymbol{n}}\,\underline{\boldsymbol{n}}(\underline{\boldsymbol{m}}\,\underline{\boldsymbol{m}}\boldsymbol{:}\boldsymbol{A})+\underline{\boldsymbol{m}}\,\underline{\boldsymbol{m}}(\underline{\boldsymbol{n}}\,\underline{\boldsymbol{n}}\boldsymbol{:}\boldsymbol{A})] \\ & + \left[\frac{2f_m^2}{3D_m}(1-S+B_1)+\frac{2f_n^2}{3D_n}(1-B-B_1-S_1)\right]\boldsymbol{A} + \left(\frac{f_m}{D_m}S+\frac{f_n}{D_n}S_1\right)(\underline{\boldsymbol{n}}\boldsymbol{N}+\boldsymbol{N}\underline{\boldsymbol{n}}) + \left(\frac{f_m}{D_m}B_1+\frac{f_n}{D_n}B\right)(\underline{\boldsymbol{m}}\boldsymbol{M}+\boldsymbol{M}\underline{\boldsymbol{m}}).\end{aligned} \tag{4.18}$$

Finally, employing the identity (D1) from Appendix D to eliminate a term proportional to the sum $\underline{\boldsymbol{n}}\,\underline{\boldsymbol{n}}(\underline{\boldsymbol{m}}\,\underline{\boldsymbol{m}}\boldsymbol{:}\boldsymbol{A})+\underline{\boldsymbol{m}}\,\underline{\boldsymbol{m}}(\underline{\boldsymbol{n}}\,\underline{\boldsymbol{n}}\boldsymbol{:}\boldsymbol{A})$, we are able to determine this part of the Leslie coefficients, which contribute to the symmetric part of the viscous stress tensor given by the phenomenological formula (2.1) (within the common factor dkT)

$$\begin{aligned}\alpha_1 &= -\frac{f_m^2}{D_m}S^2-\frac{f_n^2}{D_n}S_1^2,\\ \beta_1 &= -\frac{f_m^2}{D_m}B_1^2-\frac{f_n^2}{D_n}B^2,\\ \alpha_2+\alpha_3 &= \frac{f_m}{D_m}S+\frac{f_n}{D_n}S_1,\\ \alpha_5+\alpha_6 &= \frac{f_m^2}{D_m}S+\frac{f_n^2}{D_n}S_1+2\frac{f_m^2}{D_m}SB_1+2\frac{f_n^2}{D_n}BS_1,\\ 2\alpha_4 &= \frac{f_m^2}{3D_m}(2-2S+2B_1-6SB_1)\\ &\quad +\frac{f_n^2}{3D_n}(2-2B-2B_1-2S_1-6BS_1),\\ \beta_2+\beta_3 &= \frac{f_m}{D_m}B_1+\frac{f_n}{D_n}B,\\ \beta_5+\beta_6 &= \frac{f_m^2}{D_m}B_1+\frac{f_n^2}{D_n}B+2\frac{f_m^2}{D_m}SB_1+2\frac{f_n^2}{D_n}BS_1,\\ \mu_1+\mu_2 &= 0,\\ \mu_3+\mu_4 &= -2\frac{f_m^2}{D_m}SB_1-2\frac{f_n^2}{D_n}BS_1,\\ \mu_5 &= 0.\end{aligned} \tag{4.19}$$

We notice that, in view of Eqs. (4.10) and (2.1), only the two terms $\langle \boldsymbol{nm}(\boldsymbol{mn}\boldsymbol{:}\boldsymbol{\Omega})\rangle$ and $\langle \boldsymbol{mn}(\boldsymbol{nm}\boldsymbol{:}\boldsymbol{\Omega})\rangle$ contribute to the coefficients μ_1 and μ_2. Employing the decoupling procedure causes both these averages to factorize. The resulting products involve the terms like $\langle \boldsymbol{mn}\rangle$ and $\langle \boldsymbol{nm}\rangle$. It is obvious that the above averages, taken over the equilibrium distribution function, are equal to zero. Therefore, we have

$$\mu_1=\mu_2=0. \tag{4.20}$$

As seen, the use of the decoupling procedure appears to be too crude an approximation to grasp the coefficients μ_1 and μ_2. However, both these quantities, associated with the mixed terms, are expected to be really small compared with other Leslie coefficients. For this reason, the prediction (4.20) seems not to be a significant simplification.

To end, let us note also that, regardless of the fact that the decoupling approximation is applied, the last Onsager-Parodi relation, which states that $\mu_5=0$, is satisfied automatically.

V. THE MICROSCOPIC BALANCE EQUATION

In this section we show the method that allows for deriving the phenomenological balance equations [Eqs. (5.5)–(5.7)] introduced in Sec. II in terms of microscopic parameters. Our main task is, however, to find the missing part of the Leslie viscosity coefficients related to the antisymmetric part of the viscous stress tensor. For this purpose we will analyze a system of the PC equations (3.8)–(3.10) determining the steady-state distribution function F. We will investigate properties of these equations close to equilibrium, i.e., in the limit of a small velocity gradient. In doing this we will use a perturbation method regarding both the probability current $\boldsymbol{J}$ and the deviation δF as the first-order perturbations caused by the shear flow. The unperturbed values of F and $\boldsymbol{J}$ are, of course, $F=F_0$ and $\boldsymbol{J}=\boldsymbol{0}$, where F_0 is the equilibrium solution. It also should be noted that the method of derivation of the antisymmetric part of the stress tensor outlined in this section is, in a way, a generalization of some methods [19,26] used in the case of uniaxial symmetry.

By substituting $F=F_0+\delta F$ into the PC equations we obtain, dropping all second-order terms in perturbation, two systems of PC-type equations, denoted for the sake of brevity as PC(0) and PC(1), corresponding to the zeroth- and first-order terms, respectively. [Both systems, PC(0) and PC(1), consist clearly of three equations.] The first system of equations mentioned governs the equilibrium solution F_0 and is fully equivalent to the Hammerstein equation (3.12), which has already been throughly discussed in the preceding section. Therefore properties of the PC(0) equations are not of our interest here. For our purposes we will only make use of the second set of equations, PC(1), assuming that the equilibrium distribution function F_0 is known.

We show a straightforward transformation of the PC(1) system mentioned, which leads immediately to a system of three constitutive equations corresponding to the phenomenological equations of balance of angular momentum. Finally, by comparison of the appropriate pairs of equations, we obtain the desired microscopic expressions for the coefficients related to the antisymmetric part of the viscous stress tensor.

One may easily check that the above-mentioned, set of PC(1) equations that corresponds to the first-order perturbation has the following form:

$$l_i J_i = D_l l_i L_i \delta F - \frac{D_l}{kT}[\delta F l_i L_i U_0 + F_0 l_i L_i U[\delta F]] - F_0 l_i \omega_i, \tag{5.1}$$

$$m_i J_i = D_m m_i L_i \delta F - \frac{D_m}{kT}[\delta F m_i L_i U_0 + F_0 m_i L_i U[\delta F]] - F_0 m_i \omega_i, \tag{5.2}$$

$$n_i J_i = D_n n_i L_i \delta F - \frac{D_n}{kT}[\delta F n_i L_i U_0 + F_0 n_i L_i U[\delta F]] - F_0 n_i \omega_i, \tag{5.3}$$

where the functional $U[\delta F]$, according to Eq. (3.1), is given by the following formula:

$$U[\delta F,\boldsymbol{R}] = d\int K(\boldsymbol{R},\boldsymbol{R}')\,\delta F(\boldsymbol{R}')\,\boldsymbol{dR}'. \tag{5.4}$$

Let us now proceed to the derivation of the constitutive balance equations. For this purpose we shall start from the above-system of three PC(1) equations. The method we use is the following.

First, we multiply both sides of Eqs. (5.1), (5.2), and (5.3) by the symmetrized diads $\boldsymbol{nm}+\boldsymbol{mn}$, $\boldsymbol{nl}+\boldsymbol{ln}$, and $\boldsymbol{lm}+\boldsymbol{ml}$, respectively, and integrate them over the angular variables $\boldsymbol{dR}$. Next, we double contract the obtained system of three tensor equations with $\underline{\boldsymbol{n}}\,\underline{\boldsymbol{m}}+\underline{\boldsymbol{m}}\,\underline{\boldsymbol{n}}$, $\underline{\boldsymbol{n}}\,\underline{\boldsymbol{l}}+\underline{\boldsymbol{l}}\,\underline{\boldsymbol{n}}$ and $\underline{\boldsymbol{l}}\,\underline{\boldsymbol{m}}+\underline{\boldsymbol{m}}\,\underline{\boldsymbol{l}}$, respectively. As a result we obtain again a system of three scalar equations, which have a rather complicated forms. Fortunately, as shown in Appendix E, the obtained equations get considerably simpler after employing the expansions (3.15) and (3.13) for δF and $\boldsymbol{J}$, respectively. Finally, we arrive at the following set of equations:

$$0=(\underline{n}_p\underline{m}_q+\underline{n}_q\underline{m}_p)\langle (n_p m_q + n_q m_p) l_i \omega_i\rangle, \tag{5.5}$$

$$0=(\underline{l}_p\underline{m}_q+\underline{l}_q\underline{m}_p)\langle (l_p m_q + l_q m_p) n_i \omega_i\rangle, \tag{5.6}$$

$$0=(\underline{l}_p\underline{n}_q+\underline{l}_q\underline{n}_p)\langle (l_p n_q + l_q n_p) m_i \omega_i\rangle, \tag{5.7}$$

where $\langle\ \rangle$ denotes the equilibrium average.

We first concentrate on Eqs. (5.6) and (5.7) to recover two phenomenological equations of balance of angular momentum, Eq. (2.8) and (2.9).

Substituting the formula (3.3) for the angular velocity $\boldsymbol{\omega}$ into Eqs. (5.6) and (5.7), then making use of the identity (3.5) to eliminate the versor $\boldsymbol{l}$ from the expression determining the angular velocity $\boldsymbol{\omega}$, employing the decoupling procedure described in the previous section and finally carrying out the averaging, with the help of relations (4.15) and (4.16), we obtain

$$\left(\frac{f_m}{3}(2+S+2B_1)\underline{\boldsymbol{n}}\cdot\boldsymbol{A}+S\boldsymbol{N}\right)\cdot\underline{\boldsymbol{l}}=0 \tag{5.8}$$

$$\left(\frac{f_n}{3}(2+B-2S_1-2B_1)\underline{\boldsymbol{m}}\cdot\boldsymbol{A}+B\boldsymbol{M}\right)\cdot\underline{\boldsymbol{l}}=0, \tag{5.9}$$

where the parameters S, B, S_1, and B_1 are given by the formulas (4.17a)–(4.17d). It is not difficult to see that the above equations correspond to the appropriate balance equations (2.7) and (2.8), respectively. However, we cannot establish yet a unique relationship between those two pairs of equations, since both Eq. (5.8) and Eq. (5.9) are undetermined within certain scaling factors. Let us denote temporarily these factors by c_m and c_n, respectively. Comparison of Eq. (5.8) with Eq. (2.7) and Eq. (5.9) with Eq. (2.8) yields then immediately the coefficients γ_1, λ_1, γ_2, and λ_2:

$$\gamma_1 = c_m S, \tag{5.10}$$

$$\gamma_2 = c_m f_m (2+S+2B_1)/3, \tag{5.11}$$

$$\lambda_1 = c_n B, \tag{5.12}$$

$$\lambda_2 = c_n f_n (2+B-2S_1-2B_1)/3. \tag{5.13}$$

Therefore, our task now is to establish uniquely both factors c_m and c_n which appear in the above formulas. We can determine them making use of the fact that the coefficients γ_1 and γ_2 should satisfy the following Onsager-Parodi relations:

$$\gamma_2 = \alpha_3 + \alpha_2, \quad \lambda_2 = \beta_3 + \beta_2. \tag{5.14}$$

Indeed, one may easily check that the relations quoted above are fulfilled if and only if

$$c_m=\frac{dkT}{f_m}\left(\frac{f_m}{D_m}S+\frac{f_n}{D_n}S_1\right)\frac{3}{2+S+2B_1} \tag{5.15}$$

and

$$c_n=\frac{dkT}{f_n}\left(\frac{f_m}{D_m}B_1+\frac{f_n}{D_n}B\right)\frac{3}{2+B-2B_1-2S_1}. \tag{5.16}$$

Finally, substituting the obtained expressions for c_m and c_n into Eqs. (5.10)–(5.13) we arrive at the following formulas for the coefficients γ_1, λ_1, γ_2, and λ_2:

$$\gamma_1=\frac{dkT}{f_m}\left(\frac{f_m}{D_m}S+\frac{f_n}{D_n}S_1\right)\frac{3S}{2+S+2B_1}, \tag{5.17}$$

$$\gamma_2=dkT\left(\frac{f_m}{D_m}S+\frac{f_n}{D_n}S_1\right), \tag{5.18}$$

$$\lambda_1=\frac{dkT}{f_n}\left(\frac{f_m}{D_m}B_1+\frac{f_n}{D_n}B\right)\frac{3B}{2+B-2B_1-2S_1}, \tag{5.19}$$

$$\lambda_2=dkT\left(\frac{f_m}{D_m}B_1+\frac{f_n}{D_n}B\right). \tag{5.20}$$

Lastly we proceed to the determination of the two remaining coefficients $\gamma_3=\mu_2-\mu_1$ and $\gamma_4=\mu_3-\mu_4$.

From Eq. (4.20) we obtain immediately

$$\gamma_3=0. \tag{5.21}$$

Furthermore, the last coefficient γ_4 can be straightforwardly established if we make use of the third Onsager-Parodi relation, which imposes that

$$\gamma_4=\mu_1+\mu_2 .$$

Hence, according to Eq. (4.19), we have

$$\gamma_4=0. \tag{5.22}$$

The obtained coefficients γ_1, γ_2, γ_3, γ_4, λ_1, and λ_2 allow us to determine the antisymmetric part of the viscous stress tensor (2.1).

Employing the decoupling procedures results in vanishing of the average on the left side of Eq. (5.7). For this reason we cannot recover the third balance equation (2.9). Fortunately, we do not have to make use of this equation because two preceding relations derived, (5.6) and (5.7), together with the three Onsager-Parodi relations, have already enabled us to establish the antisymmetric part of the viscous stress tensor uniquely.

One remark concerning Eq. (5.5) is in order: It should be expected that if the decoupling approximation had not been used the appropriate averages would not vanish and, thereby, we would recover the last balance equation. For the same reasons the coefficient γ_3 would not be equal to zero.

It is easy to see that the balance equation discussed, when it exists, provides, apart from an equation for γ_3, also an equation that involves γ_2, λ_2, and γ_4. However, the latter one does not follow an additional constraint for the Leslie coefficients. This is due to the fact that Eq. (5.5) is undetermined within a certain multiplier; there are two undetermined quantities, i.e., the coefficient γ_3 and the multiplier mentioned, which have to be established. Concluding, if we had obtained the last balance equation it would provide only one equation, i.e., an equation for the determination of the coefficient γ_3.

VI. THE LESLIE VISCOSITY COEFFICIENTS

By combining the expressions (4.19), related to the symmetric part of the viscous stress, and the expressions (5.17)–(5.20), (5.22), and (5.21) we obtain finally the following formulas for the Leslie viscosity coefficients:

$$\alpha_1=-dkT\left[\frac{f_m^2}{D_m}S^2+\frac{f_n^2}{D_n}S_1^2\right],$$

$$\alpha_2=\frac{dkT}{2}\left[\frac{f_m}{D_m}S+\frac{f_n}{D_n}S_1\right]\left[1-\frac{1}{f_m}\frac{3S}{2+S+2B_1}\right],$$

$$\alpha_3=\frac{dkT}{2}\left[\frac{f_m}{D_m}S+\frac{f_n}{D_n}S_1\right]\left[1+\frac{1}{f_m}\frac{3S}{2+S+2B_1}\right],$$

$$\alpha_4=\frac{dkT}{2}\left[\frac{f_m^2}{3D_m}(2-2S+2B_1-6SB_1)\right.$$
$$\left.+\frac{f_n^2}{3D_n}(2-2B-2B_1-2S_1-6BS_1)\right],$$

$$\alpha_5=\frac{dkT}{2}\left[\left(\frac{f_m^2}{D_m}-\frac{f_m}{D_m}\right)S+\left(\frac{f_n^2}{D_n}-\frac{f_n}{D_n}\right)S_1\right.$$
$$\left.+2\frac{f_m^2}{D_m}SB_1+2\frac{f_n^2}{D_n}BS_1\right],$$

$$\alpha_6=\frac{dkT}{2}\left[\left(\frac{f_m^2}{D_m}+\frac{f_m}{D_m}\right)S+\left(\frac{f_n^2}{D_n}+\frac{f_n}{D_n}\right)S_1\right.$$
$$\left.+2\frac{f_m^2}{D_m}SB_1+2\frac{f_n^2}{D_n}BS_1\right],$$

$$\beta_1=-dkT\left[\frac{f_m^2}{D_m}B_1^2+\frac{f_n^2}{D_n}B^2\right],$$

$$\beta_2=\frac{dkT}{2}\left[\frac{f_m}{D_m}B_1+\frac{f_n}{D_n}B\right]\left[1-\frac{1}{f_n}\frac{3B}{2+B-2B_1-2S_1}\right],$$

$$\beta_3=\frac{dkT}{2}\left[\frac{f_m}{D_m}B_1+\frac{f_n}{D_n}B\right]\left[1+\frac{1}{f_n}\frac{3B}{2+B-2B_1-2S_1}\right],$$

$$\beta_5=\frac{dkT}{2}\left[\left(\frac{f_m^2}{D_m}-\frac{f_m}{D_m}\right)B_1+\left(\frac{f_n^2}{D_n}-\frac{f_n}{D_n}\right)B\right.$$
$$\left.+2\frac{f_m^2}{D_m}SB_1+2\frac{f_n^2}{D_n}BS_1\right],$$

$$\beta_6=\frac{dkT}{2}\left[\left(\frac{f_m^2}{D_m}+\frac{f_m}{D_m}\right)B_1+\left(\frac{f_n^2}{D_n}+\frac{f_n}{D_n}\right)B\right.$$
$$\left.+2\,\frac{f_m^2}{D_m}SB_1+2\,\frac{f_n^2}{D_n}BS_1\right],$$

$$\mu_1=\mu_2=0,$$

$$\mu_3=\mu_4=-dkT\left[\frac{f_m^2}{D_m}SB_1+\frac{f_n^2}{D_n}BS_1\right],$$

$$\mu_5=0.$$

It should be noted that both order parameters $\langle F_{02}^2\rangle$ and $\langle F_{20}^2\rangle$, which are involved by the above formulas, are expected to be small compared with $\langle F_{00}^2\rangle$ and $\langle F_{22}^2\rangle$. This is due to the fact that the first two averages describe rather residual ordering and vanish completely in the case of ideal biaxial alignment. Therefore they usually may be neglected, especially when one deals with a deep biaxial phase. Notice also that the form factor f_m, according to Eq. (4.7), is negative. Having obtained the viscosity coefficients, one can determine some important quantities that characterize the flow alignment configurations in the presence of a velocity gradient field.

Carlsson *et al.* [38] and Leslie [28] showed that only six equilibrium flow configurations are available and occur in pairs with one of the directors perpendicular to the plane of shear and other two in the plane of shear. Each of these configurations is characterized by an appropriate flow alignment angle. Let us denote these angles, corresponding to the flows with the directors $\underline{\boldsymbol{n}}$, $\underline{\boldsymbol{m}}$, and $\underline{\boldsymbol{l}}$ perpendicular to the plane of shear, by χ_n, χ_m, and χ_l, respectively. Accordingly, the flow alignment angles are determined by

$$-\cos 2\chi_m\equiv 1/\tau_1=\frac{\gamma_1}{\gamma_2},$$

$$-\cos 2\chi_n\equiv 1/\tau_2=\frac{\lambda_1}{\lambda_2},$$

$$-\cos 2\chi_l\equiv 1/\tau_3=\frac{\gamma_1+\gamma_3+\lambda_1}{\gamma_2+\gamma_4-\lambda_2},$$

provided that the inequalities

$$|\tau_1|>1,\quad |\tau_2|>1,\quad |\tau_3|>1$$

are fulfilled. Note also that the first ratio, τ_1, coincides with the parameter λ, which is used in the uniaxial case.

To complete this section we make use of the obtained formulas for the Leslie coefficients to express the ratios τ_1, τ_2, and τ_3 by molecular parameters. However, we do it only in the simple case of the highly ordered biaxial phase composed of very deformed molecules, for which we assume $c\gg b$. In this event, according to our remark, which has already been done, S becomes an ordinary Maier-Saupe order parameter, $B=\langle F_{22}^2\rangle$, and, obviously, $B_1\approx B$, $S_1\approx(B-S)/2$. Moreover, one expects that the rotational diffusion constant D_m associated with the rotational motion around the short molecular axis $\boldsymbol{b}$ (*tumbling*) is negligible compared with the constant D_n describing rotation around the long axis $\boldsymbol{c}$ (*spinning*). The appropriate ratios are straightforwardly found to be

$$1/\tau_1=\frac{1}{f_m}\,\frac{3S}{2+S+2B},$$

$$1/\tau_2=\frac{1}{f_n}\,\frac{3B}{2+S-B},$$

$$1/\tau_3=\frac{3}{f_mf_n}\,\frac{f_nS^2(2+S-B)+f_mB^2(2+S+2B)}{(S-B)(2+S-B)(2+S+2B)}.$$

As seen, the above formulas do not involve the diffusion constants D_m and D_n, which are a measurable input to the theory. It seems to be a serious advantage, especially considering that, as yet, the existing experimental material concerning dynamical properties of biaxial systems is very poor.

VII. THE UNIAXIAL CASE

The appropriate Leslie viscosity coefficients for the uniaxial system are obtained by setting the biaxial order parameters B and B_1 equal to zero. Moreover, since the average $\langle F_{20}^2\rangle$ is negligible compared with $\langle F_{00}^2\rangle$ in the uniaxial phase, one may put simply $S_1\approx -S/2$, where S is an usually Maier-Saupe order parameter.

For the sake of clarity, it is reasonable to differentiate two cases when the system becomes uniaxial. The first one is more general, allows for the lack of the symmetry axes of molecules, and occurs when the uniaxial phase is formed by biaxial molecules (i.e., molecules represented by ellipsoids with three different principal axes). The second case corresponds to the uniaxial phase, which consists of molecules with the symmetry axes modeled by ellipsoids of revolution. In both these cases, of course, only the six Leslie viscosity coefficients α_i have nonzero values. This is due to the global $D_{\infty h}$ symmetry of the uniaxial system.

If we deal with the first of both mentioned cases, the six viscosity coefficients take the following forms:

$$\alpha_1=-dkT\left[\frac{f_m^2}{D_m}+\frac{f_n^2}{4D_n}\right]S^2,$$

$$\alpha_2=\frac{dkT}{D_m}\,\frac{S}{2}\left[f_m-\frac{3S}{2+S}\right]-dkT\frac{f_n}{D_n}\,\frac{S}{4}\left[1-\frac{1}{f_m}\,\frac{S}{2+S}\right],$$

$$\alpha_3=\frac{dkT}{D_m}\,\frac{S}{2}\left[f_m+\frac{3S}{2+S}\right]-dkT\frac{f_n}{D_n}\,\frac{S}{4}\left[1+\frac{1}{f_m}\,\frac{S}{2+S}\right],$$

$$\alpha_4=\frac{dkT}{2}\left[\frac{2}{3}\left(\frac{f_m^2}{D_m}+\frac{f_n^2}{D_n}\right)-\frac{1}{3}\left(2\frac{f_m^2}{D_m}-\frac{f_n^2}{D_n}\right)S\right],$$

$$\alpha_5=dkT\left[\frac{f_m(f_m-1)}{2D_m}-\frac{f_n(f_n-1)}{4D_n}\right]S,$$

$$\alpha_6=dkT\left[\frac{f_m(f_m+1)}{2D_m}-\frac{f_n(f_n+1)}{4D_n}\right]S.$$

Apart from terms proportional to $1/D_m$ the above formulas contain additional terms proportional to $1/D_n$. The presence of the latter is not surprising and results from the fact that the molecules are in fact three-dimensional objects and have also rotational degree of freedom around their long molecular axes, which causes additional movement resistance. According to the Einstein formulas the resulting friction is inversely proportional to the appropriate rotational diffusion coefficient D_n. Moreover, it is intuitively understood that all residual effects related to rotational motion around the long axis depend on the level of molecular anisotropy, whose measure is a value of the form factor f_n. We expect that regardless of the value of D_n the effects mentioned are greater the more deformed the molecules composing the nematic phase are. In particular, when the molecules have symmetry axes the existence of the rotational degree of freedom mentioned does not influence the Leslie coefficients. (More precisely, this influence manifests only through the diffusion constants D_m involved by the six Leslie coefficients.)

For a typical nematic molecule the value of the rotational diffusion coefficient D_m characterizing the movement around the axis perpendicular to the long molecular axis is considerably smaller than the D_n coefficient. (For example, the NMR study of MBBA (4-methoxybenzylidene-4′-butylaniline) shows [39] that in the nematic phase D_m is about two orders of magnitude smaller than D_n.) Therefore all terms proportional to $1/D_n$ may be neglected. However, they should be taken into account when the considered nematic liquid crystal consists of molecules that are not excessively elongated and both coefficients D_n and D_m are of the same order of magnitude.

Note also that, in view of the above formulas for the Leslie viscosities, the ratio D_m/D_n is a quantity that provides information that justifies an approximation consisting in neglecting the rotational degree of freedom around the long molecular axis. Indeed, if $D_m/D_n \ll 1$ we are guaranteed that such an approximation is really reasonable.

When the nematic phase is formed by the molecules having the symmetry axes the problem gets simpler. Putting $a=b$ we obtain the following relation between the form factors: $f_l=f_m=-f$ and $f_n=0$, where $f=(p^2-1)/(p^2+1)$ and $p=c/a$ is the axis ratio of an ellipsoid of revolution. Thus, all terms proportional to f_n vanish. If we additionally put $f=1$ (thin rods), the Leslie coefficients become identical to those obtained by Marrucci [20]. Note that the Miesowicz viscosities calculated based on the formulas proposed by Marrucci are in agreement with the experimental evidence in spite of all simplifying procedures he applied.

VIII. SUMMARY

In this paper we present a method of calculation of viscosity coefficients of biaxial nematic liquid crystals based on the microscopic approach. The method we propose is consistent with the two-director continuum theory by Ericsen and Leslie. The obtained viscosity coefficients are expressed in terms of the suspension parameters such as order parameters, number density, temperature, and diffusion constants and satisfy the four Onsager-Parodi relations.

To obtain the symmetric part of the viscous stress tensor we investigate the change in the Helmholtz free energy functional $\mathcal{F}[F]$ caused by the shear flow. Next, like several authors in the case of uniaxial system, we analyze an appropriate kinetic equation of the Fokker-Planck type in order to derive the antisymmetric part of the viscous stress. However, we use the kinetic equation written in a form equivalent to the continuity equation, which involves the probability current $\boldsymbol{J}$. Such a manner, i.e., making use of the system of the three PC equations, proves to be a crucial one in the problem of the derivation of the viscosity coefficients in the case of biaxial nematic liquid crystals. The same quantities seemed out of reach using the scalar form of the Fokker-Planck equation. What is more, the presented method consisting in employing a system of PC equations can be also useful with dealing with other problems related to properties of biaxial systems.

No assumption concerning the rotational diffusion coefficients D_l, D_m, and D_n has been made. Also, we do not restrict ourselves to a certain type of the pair-interaction potential. Therefore presented results are quite general. The applicability of the derived formulas for the viscosity coefficients is not narrowed in spite of the fact that the Jefferey formula (3.3), valid for ellipsoids only, is used during the calculations. The assumption is, of course, that the molecules may be approximated by ellipsoids. Thus, all information concerning the shape is reduced to the three geometrical parameters f_l, f_m, and f_n, which describe the anisotropy of an ellipsoid. Although such an approximation seems to be a rather crude one, a similar treatment in the case of the uniaxial nematics proved to be quite satisfactory.

The presented formulas may be easily applied to the special case where the uniaxial system is composed of molecules with symmetry axes by setting all order parameters, $\langle F_{20}^2\rangle$, $\langle F_{02}^2\rangle$, and $\langle F_{22}^2\rangle$, and the form factor f_n equal to zero. Thus obtained Leslie coefficients are similar to those proposed by Marrucci in Ref. [20]. The difference is that the latter do not contain the form factor f, which makes our results more realistic. In particular, we predict the coefficient α_6 has a nonzero value. In the limiting case, when $f=1$, this difference vanishes.

Another important result consists in the fact that anisotropy of molecular shape typical for biaxial molecules, measured by a value of the form factor f_n, influences all Leslie coefficients even when the system possesses the uniaxial symmetry $D_{\infty h}$.

The main mathematical simplification applied during calculations concerns the decoupling procedure. It consist in expressing the averages of fourth-rank tensors in terms of the appropriate averages of second-rank tensors. As a consequence the obtained viscosity coefficients are expressed in terms of four order parameters being averages of the second-rank invariants F_{ij}^2 A similar approximation, originally proposed by Doi [18], was also used in the paper by Marrucci in calculations of the Leslie coefficients in the case of a uniaxial system. In spite of the mentioned decoupling approximations the viscosity coefficients derived by Marrucci are in agreement with the experimental data to a satisfactory extent. Therefore it may be expected that the formulas proposed in this paper are suitable for predicting viscous properties of biaxial systems.

In conclusion, note that the methods developed here are not intended to be complete and final; we hope that the presented method of obtaining of the Leslie viscosity coefficients will be the starting point for further investigations of viscous properties of the biaxial phase.

APPENDIX A

As a result of action of the angular momentum operator on three versors $\boldsymbol{l}$, $\boldsymbol{m}$, and $\boldsymbol{n}$ we obtain

$$L_i l_j = \epsilon_{ijk} l_k, \quad L_i n_j = \epsilon_{ijk} n_k, \quad L_i m_j = \epsilon_{ijk} m_k.$$

In order to obtain the final result we make also use of the following properties of the operator $\boldsymbol{L}$:

$$m_i L_i l_j = n_j, \quad m_i L_i n_j = -l_j, \quad m_i L_i m_j = 0, \tag{A1a}$$

$$n_i L_i l_j = -m_j, \quad n_i L_i n_j = 0, \quad n_i L_i m_j = l_j, \tag{A1b}$$

$$l_i L_i l_j = 0, \quad l_i L_i n_j = m_j, \quad l_i L_i m_j = -n_j. \tag{A1c}$$

The equilibrium mean-field potential $U_0(\boldsymbol{R})$ may be written in terms of directors $(\boldsymbol{l}, \boldsymbol{m}, \boldsymbol{n})$ and $(\underline{\boldsymbol{l}}, \underline{\boldsymbol{m}}, \underline{\boldsymbol{n}})$. In general U_0 is a sum consisting of terms of the following form:

$$\prod_{i,j=1}^{3} (\boldsymbol{\xi}^{(i)} \cdot \boldsymbol{\zeta}^{(j)})^{\alpha_{ij}}, \tag{A2}$$

where $\boldsymbol{\xi}^{(1)} = \underline{\boldsymbol{l}}$, $\boldsymbol{\xi}^{(2)} = \underline{\boldsymbol{m}}$, $\boldsymbol{\xi}^{(3)} = \underline{\boldsymbol{n}}$ and $\boldsymbol{\zeta}^{(1)} = \boldsymbol{l}$, $\boldsymbol{\zeta}^{(2)} = \boldsymbol{m}$, $\boldsymbol{\zeta}^{(3)} = \boldsymbol{n}$. Since the potential U_0 is an even function under the operations $\boldsymbol{\xi}^{(i)} \rightarrow -\boldsymbol{\xi}^{(i)}$ and $\boldsymbol{\zeta}^{(i)} \rightarrow -\boldsymbol{\zeta}^{(i)}$ for each i, the exponents α_{ij} must obey the condition that both sums $\Sigma_j \alpha_{ij}$ and $\Sigma_i \alpha_{ij}$ are even numbers for $i,j = 1,2,3$.

In order to calculate the average $\langle l_s l_j L_j U_0 \rangle$ we first inquire into the action of the differential operator $l_i L_i$ on the selected term (A2) of the expansion of U_0.

Using the rules quoted in Eqs. (A1a)–(A1c) we obtain

$$\begin{aligned} l_s L_s \prod_{p,q=1}^{3} (\boldsymbol{\xi}^{(p)} \cdot \boldsymbol{\zeta}^{(q)})^{\alpha_{pq}} &= \prod_{p,q=1}^{3} (\boldsymbol{\xi}^{(p)} \cdot \boldsymbol{\zeta}^{(q)})^{\alpha_{pq}} \sum_i \, [\alpha_{i3} (\boldsymbol{\xi}^{(i)} \cdot \boldsymbol{n})^{-1} \boldsymbol{\xi}^{(i)} \cdot \boldsymbol{m} \\ &\quad - \alpha_{i2} (\boldsymbol{\xi}^{(i)} \cdot \boldsymbol{m})^{-1} \boldsymbol{\xi}^{(i)} \cdot \boldsymbol{n}]. \end{aligned} \tag{A3}$$

It is obvious that after multiplying the above expression by l_s we obtain a function belonging to the space $\Gamma_\perp$, which is orthogonal to Γ. Hence, the average $\langle l_s l_j L_j U_0 \rangle$ taken over the equilibrium distribution function F_0, which is an element of the Γ space, vanishes.

Applying similar arguments one can show that also the two remaining averages $\langle n_s n_j L_j U_0 \rangle$ and $\langle m_s m_j L_j U_0 \rangle$ vanish.

APPENDIX B

Before we proceed to calculate the appropriate integrals involving J_i, we investigate some general properties of the probability current that is assumed to be linear in perturbation represented by $\boldsymbol{A}$ and $\boldsymbol{\Omega}$.

There are two restrictions that considerably limit the family of all J_i functions we should take into account: Firstly, we require the probability current to obey the condition $L_i J_i = 0$. Secondly, the projections $l_i J_i$, $m_i J_i$, and $n_i J_i$ must be elements of the Γ space. One can check that the most general form of the current J_i that satisfies the conditions quoted above is the following:

$$\begin{aligned} J_i(\boldsymbol{R}) &= l_i j_l \Phi_l(\boldsymbol{R}) + m_i j_m \Phi_m(\boldsymbol{R}) + n_i j_n \Phi_n(\boldsymbol{R}) \\ &\quad + l_i(\boldsymbol{m} \cdot \boldsymbol{\Omega} \cdot \boldsymbol{n}) \Upsilon_l(\boldsymbol{R}) + m_i(\boldsymbol{n} \cdot \boldsymbol{\Omega} \cdot \boldsymbol{l}) \Upsilon_m(\boldsymbol{R}) \\ &\quad + n_i(\boldsymbol{l} \cdot \boldsymbol{\Omega} \cdot \boldsymbol{m}) \Upsilon_n(\boldsymbol{R}) + l_i(\boldsymbol{l} \cdot \boldsymbol{A} \cdot \boldsymbol{l}) \Psi_l(\boldsymbol{R}) \\ &\quad + m_i(\boldsymbol{m} \cdot \boldsymbol{A} \cdot \boldsymbol{m}) \Psi_m(\boldsymbol{R}) + n_i(\boldsymbol{n} \cdot \boldsymbol{A} \cdot \boldsymbol{n}) \Psi_n(\boldsymbol{R}), \end{aligned} \tag{B1}$$

where j_l, j_m, and j_n are constants composed by the invariants of $\boldsymbol{A}$ and $\boldsymbol{\Omega}$; the functions $\Phi_l(\boldsymbol{R})$, $\Phi_m(\boldsymbol{R})$, and $\Phi_n(\boldsymbol{R})$, and the products $(\boldsymbol{m} \cdot \boldsymbol{\Omega} \cdot \boldsymbol{n}) \Upsilon_l(\boldsymbol{R})$, . . . , $(\boldsymbol{n} \cdot \boldsymbol{A} \cdot \boldsymbol{n}) \Psi_n(\boldsymbol{R})$ belong to the Γ space.

Let us consider the following integral:

$$\mathcal{I}_{pq} = \int (m_p n_q + m_q n_p) l_i J_i(\boldsymbol{R}) \boldsymbol{dR}. \tag{B2}$$

Substituting for the current J_i in Eq. (B1) we obtain

$$\begin{aligned} \mathcal{I}_{pq} = \int (m_p n_q + m_q n_p) [& j_l \Phi_l(\boldsymbol{R}) + \boldsymbol{m} \cdot \boldsymbol{\Omega} \cdot \boldsymbol{n} \Upsilon_l(\boldsymbol{R}) \\ &+ \boldsymbol{l} \cdot \boldsymbol{A} \cdot \boldsymbol{l} \Psi_l(\boldsymbol{R})] \boldsymbol{dR}. \end{aligned} \tag{B3}$$

One may straightforwardly check that the integrand is an even function with respect to the operation $\boldsymbol{l} \rightarrow -\boldsymbol{l}$ and an odd function with respect to the operations $\boldsymbol{m} \rightarrow -\boldsymbol{m}$ and $\boldsymbol{n} \rightarrow -\boldsymbol{n}$. Thus, the integral $\mathcal{I}_{pq}$ vanishes.

In an analogous way we obtain also

$$\int (l_p m_q + l_q m_p) n_i J_i(\boldsymbol{R}) \boldsymbol{dR} = 0,$$

$$\int (n_p l_q + n_q l_p) m_i J_i(\boldsymbol{R}) \boldsymbol{dR} = 0.$$

APPENDIX C

The basic functions F^l_{ij} generating the Γ solution space for the one-particle distribution function of the biaxial system are given by the following formula:

$$F^l_{ij} = (\sqrt{2})^{-2-\delta_{i0}-\delta_{0j}} \sum_{\sigma\rho \in \{1,-1\}} (-1)^{l(\rho-\sigma)/2} D^{(l)}_{\rho i, \sigma j}(\boldsymbol{R}), \tag{C1}$$

where l, i, j are integer numbers and $\boldsymbol{R}$ is the rotation parametrized by three Euler angles. D^l_{ij} are the standard rotation matrix elements [30].

The functions F^l_{ij} obey the following orthonormality relations:

$$\int d\boldsymbol{R} F^l_{ij}(\boldsymbol{R}) F^k_{mn}(\boldsymbol{R}) = \delta_{lk} \delta_{im} \delta_{jn} \frac{8\pi^2}{2l+1}.$$

Thus, according to Eq. (C1), F^2_{00} is given by

$$F_{00}^{2}=\frac{3}{2}(\cos^{2}\theta-1/3).$$

Three other functions, F_{20}^{2}, F_{02}^{2}, and F_{22}^{2} which appear in the definition of the order parameters, expressed in terms of Euler angles have the following forms:

$$F_{20}^{2}=\frac{\sqrt{3}}{2}\sin^{2}\theta\cos 2\varphi,$$

$$F_{02}^{2}=\frac{\sqrt{3}}{2}\sin^{2}\theta\cos 2\psi,$$

$$F_{22}^{2}=\frac{1}{2}(1+\cos^{2}\theta)\cos 2\varphi\cos 2\psi-\cos\theta\sin 2\varphi\sin 2\psi.$$

As seen from the definition, the average $\langle F_{00}^{2}\rangle$ is the commonly used in the uniaxial case Maier-Saupe order parameter.

Averages of F_{02}^{2} and F_{22}^{2} take nonzero values only if the system possesses the D_{2h} (or lower) symmetry and vanish in the case of the $D_{\infty h}$ symmetry possessed by the uniaxial system. The $\langle F_{20}^{2}\rangle$ may take nonzero values even when the system possesses the uniaxial symmetry. However, it is usually very small compared with a value of the parameter S. Note also that both averages $\langle F_{20}^{2}\rangle$ and $\langle F_{02}^{2}\rangle$ vanish in the case of the ideal biaxial alignment.

APPENDIX D

To eliminate a term proportional to $(n_i n_j m_k m_p A_{kp}+m_i m_j n_k n_p A_{kp})$ from Eq. (4.18) we use the following identity [4,6]:

$$\begin{aligned}(n_i n_j m_k m_p A_{kp}+m_i m_j n_k n_p A_{kp})\\ =A_{ij}+(n_i m_j+m_i n_j)m_k n_p A_{kp}-(m_i m_k A_{jk}+m_j m_k A_{ik})\\ -(n_i n_k A_{jk}+n_j n_k A_{ik})+(n_k n_p A_{kp}+m_k m_p A_{kp})\delta_{ij}.\end{aligned} \tag{D1}$$

APPENDIX E

Let us consider the first equation, (5.1), of the PC(1) system. Multiplying it by $\boldsymbol{nm}+\boldsymbol{mn}$ and integrating over the angular variables $\boldsymbol{dR}$ we obtain the following equation:

$$\begin{aligned}kT\int(m_p n_q+m_q n_p)l_i J_i(\boldsymbol{R})\boldsymbol{dR}\\ =-D_l\int(m_p n_q+m_q n_p)\delta F l_i L_i U_0\boldsymbol{dR}\\ -D_l\int(m_p n_q+m_q n_p)F_0 l_i L_i U[\delta F]\boldsymbol{dR}\\ +kTD_l\int(m_p n_q+m_q n_p)l_i L_i\delta F\boldsymbol{dR}\\ -kT\int(m_p n_q+m_q n_p)F_0 l_i\omega_i\boldsymbol{dR}.\end{aligned} \tag{E1}$$

First of all, we see that, according to the results from Appendix B, the integral involving $\boldsymbol{J}$ vanishes.

In order to calculate the first integral form the right side of Eq. (E1) we investigate properties of the following product:

$$(m_p n_q+m_q n_p)l_i L_i U_0. \tag{E2}$$

According to Eq. (A3), in the expansion of the above expression only terms of the following form appear:

$$\prod_{p,q=1}^{3}(\boldsymbol{\xi}^{(p)}\cdot\boldsymbol{\zeta}^{(q)})^{\alpha_{pq}}(\boldsymbol{\xi}^{(k)}\cdot\boldsymbol{n})^{-1}\boldsymbol{\xi}^{(k)}\cdot\boldsymbol{m}(m_p n_q+m_q n_p)$$

and

$$\prod_{p,q=1}^{3}(\boldsymbol{\xi}^{(p)}\cdot\boldsymbol{\zeta}^{(q)})^{\alpha_{pq}}(\boldsymbol{\xi}^{(k)}\cdot\boldsymbol{m})^{-1}\boldsymbol{\xi}^{(k)}\cdot\boldsymbol{n}(m_p n_q+m_q n_p),$$

where α, β, and γ are even numbers. Hence, the product Eq. (E2) is clearly invariant with respect to the operations $\boldsymbol{l}\rightarrow-\boldsymbol{l}$, $\boldsymbol{m}\rightarrow-\boldsymbol{m}$, and $\boldsymbol{n}\rightarrow-\boldsymbol{n}$.

Next, we analyze symmetry properties of the perturbation δF. According to Eq. (3.15) we have

$$\delta F=-\delta R_i L_i F_0. \tag{E3}$$

Making use of the fact that δR_i may be written down as

$$\delta R_i=l_i\delta R_l+m_i\delta R_m+n_i\delta R_n, \tag{E4}$$

where δR_l, δR_m, and δR_n are certain constants, we have

$$\delta R_i L_i F_0=(\delta R_l l_i L_i+\delta R_m m_i L_i+\delta R_n n_i L_i)F_0. \tag{E5}$$

Since the equilibrium distribution function F_0 is an element of the Γ space, it may be easily verified that $\delta R_i L_i F_0$ consists of terms being odd functions with respect to one of the versors $\boldsymbol{l}$, $\boldsymbol{m}$, $\boldsymbol{n}$ and even functions with respect to the two remaining versors. Therefore, considering the symmetry of the product of δF and the expression (E2) with regard to the versors $\boldsymbol{l}$, $\boldsymbol{m}$, and $\boldsymbol{n}$ we see that the first integral is equal to zero.

Let us now proceed to calculate the second integral. We see that, according to the definition (3.1) of the functional U, the expression

$$U[\delta F,\boldsymbol{R}]=d\int K(\boldsymbol{R},\boldsymbol{R}')\delta F(\boldsymbol{R}')\boldsymbol{R}',$$

has the same symmetry properties with regard to the versors $\boldsymbol{l}$, $\boldsymbol{m}$, and $\boldsymbol{n}$ like the perturbation δF. Therefore, one can easily check that an action of the differential operator $l_i L_i$ on $U[\delta F]$ leads to an expression that is an even function of $\boldsymbol{l}$, $\boldsymbol{m}$, and $\boldsymbol{n}$. Analyzing the appropriate symmetry properties of the product $(m_p n_q+m_q n_p)l_i L_i U[\delta F]F_0$, we find out that the second integral must vanish.

Finally, we proceed to the third integral. $l_i L_i\delta F$ is an even function with respect to the versors $\boldsymbol{m}$, and $\boldsymbol{n}$ and an odd function with respect to the versor ***l***. Thus, due to symmetry properties of the product $(m_p n_q + m) l_i L_i \delta F$ the third integral is also equal to zero. The only nonzero term is the last integral. Therefore, contracting Eq. (E1) with the tensor $\underline{\boldsymbol{m}}\,\underline{\boldsymbol{n}}+\underline{\boldsymbol{n}}\,\underline{\boldsymbol{m}}$ we derive the Eq. (5.5). In an analogous way one can easily verify also that the procedure described in Sec. V transforms Eqs. (5.2) and (5.3) into Eqs. (5.6) and (5.7), respectively.

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