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Viscous properties of nematic liquid crystals composed of biaxial molecules

Marcin Fiałkowski
Jagiellonian University, Institute of Physics, ulica Reymonta 4, 30-059 Cracow, Poland

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This paper presents a further improvement of the mean-field method of obtaining the Leslie viscosity coefficients of biaxial nematic liquid crystals presented in our last paper [M. Fialkowski, Phys. Rev. E **55**, 2902 (1997)]. We carry out the calculations without using simplifying procedures employed in the cited paper. The viscosities presented are expressed by suspension parameters such as second- and fourth-rank order parameters, three diffusion constants, temperature, number density, and certain factors depending on the shapes of the molecules. Viscous properties of uniaxial phase composed by biaxial molecules are also considered. We show that our results recover existing formulas for six Leslie viscosities obtained for the uniaxial system. The problem of the rotational diffusion tensor has been investigated within the hydrodynamic approximation. The rotational diffusion coefficients have been expressed by the common shear viscosity η. As an example, we also present the viscosities calculated numerically for a mean-field model of biaxial nematic liquid crystals.
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I. INTRODUCTION

In the previous paper [1] we provided a systematic method of deriving the viscosities of biaxial nematic liquid crystals. The method is based, in general, on the mean-field molecular approach developed by Doi [2] and Kuzuu and Doi [3] for uniaxial nematics. We have adopted their method of calculating the viscosities for biaxial systems. In this way, the two-director phenomenological theory proposed by Carlsson, Leslie, and Laverty [4] and Leslie, Laverty, and Carlsson [5,6] was recovered. In particular, all the Leslie viscosity coefficients were calculated in terms of suspension parameters such as order parameters, diffusion constants, temperature, and number density.

To proceed with the calculations, however, we employed a mathematical approximation consisting in decoupling all the averages of fourth-rank tensors and expressing them using the appropriate averages of the second-rank tensors. As a consequence, the derived formulas for the viscosity coefficients involved only second-rank order parameters. In the uniaxial limit, they recovered six Leslie viscosities obtained by Marrucci [7].

Although the treatment presented in our previous work was, in general, successful and allowed us to derive all the viscosity coefficients, the decoupling procedure used during the calculations is rather rough and may lead, in the worst case, to an error of the order of 100%. Perhaps the most evident failure caused by the use of the decoupling approximation was the prediction that two viscosities, μ_1 and μ_2, are equal to zero.

The first purpose of this paper is therefore to improve the method by eliminating the above simplification. As a result, we obtain exact formulas for the Leslie viscosities expressed in terms of both second- and fourth-rank order parameters and are free from the weaknesses caused by the use of the decoupling procedure.

Moreover, the limit of the derived expressions corresponding to the uniaxial symmetry, $D_{\infty h}$ is thoroughly discussed. It is shown that the formulas presented for the Leslie coefficients may be regarded as a natural generalization of the existing formulas, which have recently been obtained within the framework of uniaxial theory. Furthermore, we demonstrate that the above-mentioned uniaxial formulas may be easily improved in such a way that some effects related to the residual biaxiality of the molecules are taken into account.

In this paper we deal also with the rotational diffusion coefficients characterizing the Brownian motion of biaxial molecules. We show that if molecular shapes are approximated by ellipsoids it is possible to express each diffusion coefficient with the common viscosity η and certain geometrical factors depending on anisotropy of the ellipsoid. Although, as we show, such an approach to the problem of rotational motion of the molecule is rather rough, it enables us to compare relative magnitudes of the viscosity coefficients.

This paper is organized as follows. In Sec. II we outline the two-director formulation of the phenomenological theory for biaxial nematic liquid crystals, calculate the symmetric part of the viscous stress tensor, and derive the equations of balance of angular momentum and, as a main result, we present the exact formulas for the Leslie viscosity coefficients. Next, in Sec. III, we investigate our results in the limit of uniaxial symmetry. In Sec. IV we deal with the problem of the rotational diffusion tensor in the framework of hydrodynamic approximation. Eventually, in Sec. V we present sample calculations of the viscosity coefficients performed for a mean-field model of a biaxial nematic liquid crystal, in which pair interaction between molecules is described by the Lennard-Jones type potential. Some comments on the results presented are given in the concluding section, VI.

II. THE STRESS TENSOR AND THE LESLIE VISCOSITY COEFFICIENTS

A. The continuum theory

The phenomenological description of viscosity for incompressible biaxial nematic liquid crystals has recently been proposed by Leslie and co-workers [5,6] within the framework of the two-director continuum theory. According to this theory, the viscous stress tensor σ_{ij} is expressed in terms of two orthogonal vectors, $\underline{\boldsymbol{m}}$ and $\underline{\boldsymbol{n}}$, describing the biaxiality of the system,

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

where the vectors $\boldsymbol{N}$ and $\boldsymbol{M}$ are defined as

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

with $\boldsymbol{\Omega}$ and $\boldsymbol{A}$ being antisymmetric and symmetric parts of the velocity gradient tensor ∂_iv_j, respectively,

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

The coefficients α_i, β_i, and μ_i are called the Leslie viscosity coefficients and are linked by the four Onsager-Parodi relations

$$\begin{aligned}&\alpha_3+\alpha_2=\alpha_6-\alpha_5,\\&\beta_3+\beta_2=\beta_6-\beta_5,\\&\mu_1+\mu_2=\mu_4-\mu_3,\\&\mu_5=0.\end{aligned}\tag{2.2}$$

Thus, we have 12 linearly independent viscosity coefficients.

The balance of angular momentum is given by the following set of three scalar equations:

$$(\gamma_1N_i+\gamma_2A_{ij}\underline{n}_j)\underline{l}_i=0,\tag{2.3}$$

$$(\lambda_1M_i+\lambda_2A_{ij}\underline{m}_j)\underline{l}_i=0,\tag{2.4}$$

$$[(\gamma_1+\gamma_3+\lambda_1)N_i+(\gamma_2+\gamma_4-\lambda_2)A_{ij}\underline{n}_j]\underline{m}_j=0,\tag{2.5}$$

where $\underline{\boldsymbol{l}}=\underline{\boldsymbol{m}}\times\underline{\boldsymbol{n}}$. The coefficients appearing in the above equations are linear combinations of the Leslie viscosities

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

$$\lambda_1=\beta_3-\beta_2,\quad \lambda_2=\beta_6-\beta_5,$$

$$\gamma_3=\mu_2-\mu_1,\quad \gamma_4=\mu_4-\mu_3.$$

B. The viscous stress tensor

We consider an incompressible nematic biaxial liquid crystal consisting of biaxial molecules. It is assumed that the molecules are modeled by ellipsoids of the axial ratios $a:b:c$, where $c\geqslant a\geqslant b$. The orientation of the selected molecule is defined by the rotation $\boldsymbol{R}$ carrying the fixed reference frame $(\underline{\boldsymbol{l}},\underline{\boldsymbol{m}},\underline{\boldsymbol{n}})$ into a frame $(\boldsymbol{l},\boldsymbol{m},\boldsymbol{n})$ fixed in this molecule. The unit vectors $\boldsymbol{l}$, $\boldsymbol{m}$, and $\boldsymbol{n}$ coincide with the symmetry axes of the ellipsoids, $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$, respectively. The probability that the molecule has orientation $\boldsymbol{R}$ is given by the one-particle distribution function $F=F(\boldsymbol{R})$.

To describe dynamics of the molecules we apply the diffusional model, where the reorientation is treated as a stochastic Brownian precess. The rotational movement around the three principal axes is characterized by the diffusion tensor D_{ij}. Since it is assumed that the stochastic motion of the selected molecule proceeds around all three axes independently, the tensor D_{ij} is diagonal in the molecular frame of reference. The appropriate diagonal elements are denoted D_l, D_m, and D_n. They correspond, respectively, to the diffusion coefficients around the $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$ principal axes of the ellipsoid.

In order to derive the viscous stress tensor σ_{ij} from the molecular level, we use an improved version of the method originally used by Kuzuu and Doi [3] in the case of uniaxial nematics. The method we use essentially consists of separate calculations of the symmetric and the antisymmetric parts of the viscous stress tensor. It was thoroughly described in [1]. Here, we quote only the main results obtained in our previous work.

The first important result derived was the formula for the symmetric part of the viscous stress tensor expressed in terms of molecular parameters,

$$2\sigma_{ij}^{\mathrm{sym}}/dk_BT=2A\langle n_in_jn_kn_p\rangle A_{kp}+2B\langle m_im_jm_km_p\rangle A_{kp}+C\langle n_im_jn_km_pA_{kp}+n_jm_in_km_pA_{kp}\rangle-A\langle n_in_kA_{jk}+n_jn_kA_{ik}\rangle$$
$$-B\langle m_im_kA_{jk}+m_jm_kA_{ik}\rangle+A_1\langle n_in_k\Omega_{kj}+n_jn_k\Omega_{ki}\rangle+B_1\langle m_im_k\Omega_{kj}+m_jm_k\Omega_{ki}\rangle$$
$$+C_1\langle n_in_km_jm_p\Omega_{kp}+m_in_kn_jm_p\Omega_{kp}\rangle. \tag{2.6}$$

In the above expression T is the temperature, k_B is the Boltzmann constant, d stands for the number density of the system, and $\langle\rangle$ denotes the average taken over the equilibrium distribution function. The parameters A, A_1, B, B_1, C, and C_1 are defined as

$$A=-\frac{f_m^2}{D_m},\quad A_1=\frac{f_m}{D_m},\quad B=-\frac{f_n^2}{D_n},\quad B_1=\frac{f_n}{D_n},$$
$$C=-\left(\frac{f_m^2}{D_m}-\frac{f_l^2}{D_l}+\frac{f_n^2}{D_n}\right),\quad C_1=\left(\frac{f_l}{D_l}-\frac{f_m}{D_m}-\frac{f_n}{D_n}\right), \tag{2.7}$$

with the form factors f_l, f_m, and f_n,

$$f_l=\frac{b^2-c^2}{b^2+c^2},\quad f_m=\frac{a^2-c^2}{c^2+a^2},\quad f_n=\frac{a^2-b^2}{a^2+b^2}. \tag{2.8}$$

We obtained also the following set of scalar equations corresponding to the balance of angular momentum, Eqs. (2.3)–(2.5):

$$0=(\underline{n}_p\underline{m}_q+\underline{n}_q\underline{m}_p)\langle(n_pm_q+n_qm_p)l_i\omega_i\rangle, \tag{2.9}$$

$$0=(\underline{l}_p\underline{m}_q+\underline{l}_q\underline{m}_p)\langle(l_pm_q+l_qm_p)n_i\omega_i\rangle, \tag{2.10}$$

$$0=(\underline{l}_p\underline{n}_q+\underline{l}_q\underline{n}_p)\langle(l_pn_q+l_qn_p)m_i\omega_i\rangle, \tag{2.11}$$

where the vector ω_i is the angular velocity due to the shearing flow [8],

$$\boldsymbol{\omega}=-\boldsymbol{l}[\boldsymbol{m}\cdot(f_l\mathbf{A}-\boldsymbol{\Omega})\cdot\boldsymbol{n}]-\boldsymbol{m}[\boldsymbol{l}\cdot(f_m\mathbf{A}+\boldsymbol{\Omega})\cdot\boldsymbol{n}]$$
$$+\boldsymbol{n}[\boldsymbol{m}\cdot(f_n\mathbf{A}-\boldsymbol{\Omega})\cdot\boldsymbol{l}].$$

The formula (2.6) together with the three equations (2.9)–(2.11) allow one to obtain the whole viscous stress tensor and, by comparison with the appropriate phenomenological formulas, to predict the Leslie viscosity coefficients.

In our previous work, to calculate the tensor averages we applied the decoupling approximation of the form $\langle a_ib_ja_kA_{kl}b_l\rangle\approx\langle a_ib_j\rangle\langle a_kA_{kl}b_l\rangle$, $\langle a_ib_ja_k\Omega_{kl}b_l\rangle\approx\langle a_ib_j\rangle\langle a_k\Omega_{kl}b_l\rangle$, where a_i and b_i stand for the components of vectors n_i and m_i, i.e., $a_i=n_i,m_i$, $b_i=n_1,m_i$. In the present paper, we carry out the averaging without using the above-mentioned decoupling procedure. As a result, we obtain the following expression for the symmetric part of the stress tensor (within the factor $dk_BT/2$):

$$\boldsymbol{\sigma}^{sym}=2[Aa_1+Bb_1+Cc_1]\underline{\boldsymbol{n}}\underline{\boldsymbol{n}}(\underline{\mathbf{n}}\underline{\mathbf{n}}\mathbf{:A})+2[Aa_2+Bb_2+Cc_2]\underline{\mathbf{m}}\underline{\mathbf{m}}(\underline{\mathbf{m}}\underline{\mathbf{m}}\mathbf{:A})+2[A(2a_4+a_3)+B(2b_4+b_3)+C(c_3+c_4)]$$
$$\times[\underline{\mathbf{n}}\underline{\mathbf{m}}(\underline{\mathbf{n}}\underline{\mathbf{m}}\mathbf{:A})+\underline{\mathbf{m}}\underline{\mathbf{n}}(\underline{\mathbf{n}}\underline{\mathbf{m}}\mathbf{:A})]+[2A(a_5-a_3)+2B(b_5-b_3)+C(c_5-2c_3)-Ad_1-Bd_2](\underline{\mathbf{n}}\underline{\mathbf{n}}\cdot\mathbf{A}+\mathbf{A}\cdot\underline{\mathbf{n}}\underline{\mathbf{n}})$$
$$+[2A(a_6-a_3)+2B(b_6-b_3)+C(c_6-2c_3)-Ad_4-Bd_3](\underline{\mathbf{m}}\underline{\mathbf{m}}\cdot\mathbf{A}+\mathbf{A}\cdot\underline{\mathbf{m}}\underline{\mathbf{m}})-2[A(1-d_1-d_4-3a_3)$$
$$+B(1-d_2-d_3-3b_3)-3Cc_3]/3\mathbf{A}+[C_1c_7+A_1d_1+B_1d_2](\underline{\mathbf{n}}\cdot\mathbf{N}+\mathbf{N}\cdot\underline{\mathbf{n}})+[C_1c_8+A_1d_4+B_1d_3](\underline{\mathbf{m}}\cdot\mathbf{M}+\mathbf{M}\cdot\underline{\mathbf{m}}). \tag{2.12}$$

Similarly, after calculating the averages, the equations (2.9)–(2.11) take the following forms:

$$0=[X_l\underline{\mathbf{n}}\cdot\mathbf{A}+Y_l\mathbf{N}]\cdot\underline{\mathbf{m}},\quad 0=[X_n\underline{\mathbf{m}}\cdot\mathbf{A}+Y_n\mathbf{M}]\cdot\underline{\mathbf{l}},$$
$$0=[X_m\underline{\mathbf{n}}\cdot\mathbf{A}+Y_m\mathbf{N}]\cdot\underline{\mathbf{l}}, \tag{2.13}$$

with

$$X_l=f_l(2c_4+c_5+c_6),\quad Y_l=c_8-c_7,$$
$$X_n=f_n(2+d_3-2d_2-6b_6-3c_6),\quad Y_n=3(d_3+c_8),$$
$$X_m=f_m(2+d_1-2d_4-6a_5-3c_5),\quad Y_m=3(d_1+c_7).$$

The parameters a_i, b_i, c_i, and d_i, being linear combinations of the equilibrium averages of the basic functions F_{ij}^l, are quoted in Appendix B.

Each of the above quoted balance equations is undetermined up to certain multipliers c_l, c_m, and c_n, respectively. Thus, Eqs. (2.13) are equivalent to the following system of equations:

$$0=[c_lX_l\underline{\mathbf{n}}\cdot\mathbf{A}+c_lY_l\mathbf{N}]\cdot\underline{\mathbf{m}}, \tag{2.14}$$

$$0=[c_nX_n\underline{\mathbf{m}}\cdot\mathbf{A}+c_nY_n\mathbf{M}]\cdot\underline{\mathbf{l}}, \tag{2.15}$$

$$0=[c_mX_m\underline{\mathbf{n}}\cdot\mathbf{A}+c_mY_m\mathbf{N}]\cdot\underline{\mathbf{l}}. \tag{2.16}$$

To determine the multipliers, we make use of the fact that the coefficients γ_2, γ_4, and λ_2 have to obey the Onsager-

Parodi relations (2.2). Comparing Eqs. (2.14)–(2.16) with Eqs. (2.3)–(2.5), we easily find that the relations (2.2) are satisfied if and only if

$$c_m = \frac{C_1 c_7 + A_1 d_1 + B_1 d_2}{f_m(2 + d_1 - 2d_4 - 6a_5 - 3c_5)},$$

$$c_n = \frac{C_1 c_8 + A_1 d_4 + B_1 d_3}{f_n(2 + d_3 - 2d_2 - 6b_6 - 3c_6)},$$

$$c_l = \frac{C_1(c_7 - c_8) + A_1(d_1 - d_4) + B_1(d_2 - d_3)}{f_l(2c_4 + c_5 + c_6)}.$$

The above formulas allow one to determine the balance equations (2.14)–(2.16) uniquely and to establish the coefficients $\gamma_{1,2}$, $\lambda_{1,2}$ and $\gamma_{3,4}$. Having obtained the symmetric part of the stress tensor and the balance equations, we can recover the whole stress σ_{ij} and thereby calculate the viscosity coefficients.

C. The Leslie viscosity coefficients

Comparing Eqs. (2.14)–(2.16) to Eqs. (2.3)–(2.5), and the expression (2.12) to the symmetric part of the phenomenological stress tensor given by Eq. (2.1), we arrive at the following formulas for the Leslie viscosities (within the common factor $dk_BT/2$):

$$\alpha_1 = 2Aa_1 + 2Bb_1 + 2Cc_1,$$

$$\alpha_2 = [C_1 c_7 + A_1 d_1 + B_1 d_2][1 - \lambda_m^{-1}],$$

$$\alpha_3 = [C_1 c_7 + A_1 d_1 + B_1 d_2][1 + \lambda_m^{-1}],$$

$$\alpha_4 = -2[A(1 - d_1 - d_4 - 3a_3) + B(1 - d_2 - d_3 - 3b_3) - 3Cc_3]/3,$$

$$\alpha_5 = A(2a_5 - 2a_3 - d_1) + B(2b_5 - 2b_3 - d_2) + C(c_5 - 2c_3) - C_1 c_7 - A_1 d_1 - B_1 d_2,$$

$$\alpha_6 = A(2a_5 - 2a_3 - d_1) + B(2b_5 - 2b_3 - d_2) + C(c_5 - 2c_3) + C_1 c_7 + A_1 d_1 + B_1 d_2,$$

$$\beta_1 = 2Aa_2 + 2Bb_2 + 2Cc_2,$$

$$\beta_2 = [C_1 c_8 + A_1 d_4 + B_1 d_3][1 - \lambda_n^{-1}],$$

$$\beta_3 = [C_1 c_8 + A_1 d_4 + B_1 d_3][1 + \lambda_n^{-1}],$$

$$\beta_5 = A(2a_6 - 2a_3 - d_4) + B(2b_6 - 2b_3 - d_3) + C(c_6 - 2c_3) - C_1 c_8 - A_1 d_4 - B_1 d_3,$$

$$\beta_6 = A(2a_6 - 2a_3 - d_4) + B(2b_6 - 2b_3 - d_3) + C(c_6 - 2c_3) + C_1 c_8 + A_1 d_4 + B_1 d_3,$$

$$\mu_1 = -\mu_2 = \lambda_m^{-1}[C_1 c_7 + A_1 d_1 + B_1 d_2] + \lambda_n^{-1}[C_1 c_8 + A_1 d_4 + B_1 d_3] - \lambda_l^{-1}[C_1(c_7 - c_8) + A_1(d_1 - d_4) + B_1(d_2 - d_3)],$$

$$\mu_3 = \mu_4 = A(2a_4 + a_3) + B(2b_4 + b_3) + C(c_3 + c_4),$$

$$\mu_5 = 0, \tag{2.17}$$

where

$$\lambda_l = f_l \frac{2c_4 + c_5 + c_6}{c_8 - c_7},$$

$$\lambda_m = f_m \frac{2 + d_1 - 2d_4 - 6a_5 - 3c_5}{3(d_1 + c_7)},$$

$$\lambda_n = f_n \frac{2 + d_3 - 2d_2 - 6b_6 - 3c_6}{3(d_3 + c_8)}.$$

The parameters λ_l, λ_m, and λ_n are related to the coefficients γ_i and λ_i by

$$\lambda_l = \frac{\gamma_2 + \gamma_4 - \lambda_2}{\gamma_1 + \gamma_3 + \lambda_1}, \quad \lambda_n = \frac{\lambda_2}{\lambda_1}, \quad \lambda_m = \frac{\gamma_2}{\gamma_1},$$

and determine the flow alignment angles, χ_l, χ_m, and χ_n, corresponding to the flow configurations in which the plane of the shear is perpendicular to the director $\underline{\boldsymbol{l}}$, $\underline{\boldsymbol{m}}$, or $\underline{\boldsymbol{n}}$, respectively. As showed by Carlsson, Leslie, and Laverty [4] and Leslie [6], only the above-mentioned three types of configurations are possible. The appropriate flow alignment angles are given by

$$\cos 2\chi_l = -1/\lambda_l, \quad \cos 2\chi_m = -1/\lambda_m, \quad \cos 2\chi_n = -1/\lambda_n.$$

The obtained formulas for the viscosities are rather complicated. To predict the behavior of the Leslie coefficients one has to know the temperature dependences of the thirteen scalar order parameters as well as of the three rotational diffusion constants. Moreover, the form factors f_l, f_m, and f_n describing the effective anisotropy of the shape of the molecules have to be known. In our approach, they play instead a role of adjustable parameters that have to be established by fitting the theoretical predictions of the Leslie viscosities to experimental data.

It is also worth noting that if one deals with prolate biaxial molecules (rodlike), only five order parameters, namely, $\langle F_{00}^2 \rangle$, $\langle F_{22}^2 \rangle$, $\langle F_{00}^4 \rangle$, $\langle F_{22}^4 \rangle$, and $\langle F_{44}^4 \rangle$, are of practical interest, whereas the remaining eight are expected to be completely negligible in the calculations. Such a behavior of the order parameters has been confirmed by several approaches [9–12] based on the mean-field description of the biaxial phase as well as by Monte Carlo simulations [13]. This yields a significant simplification of the problem, especially when the order parameters must be determined from experiment.

III. THE LIMIT OF UNIAXIAL SYMMETRY

An important advantage of the method presented is that one can derive the uniaxial limit by simply setting the appropriate biaxial order parameters equal to zero. In this way one may easily find the viscosities for regular uniaxial nematics consisting of axially symmetrical molecules. Moreover, the transition from the D_{2h} to the $D_{\infty h}$ symmetry allows one to also obtain formulas for the Leslie coefficients describing the viscosity of the uniaxial phase composed of molecules possessing the biaxial symmetry. Such formulas seem out of reach starting from the the uniaxial approach.

When the molecules possess symmetry axes, the formulas for the Leslie coefficients describe the viscosity of a regular uniaxial nematic liquid crystal. For the molecules modeled by the ellipsoids of revolution, all the formulas for the Leslie coefficients get considerably simpler. Indeed, in this case the diffusion coefficients D_l and D_m become identical, $D_l=D_m=D_\perp$. Similarly, $f_l=f_m=-f$, where $f=(p^2-1)/(p^2+1)$ with $p=c/a$ being the ellipsoidal length-to-width ratio. The third form factor, f_n is then equal to zero. Thus, according to Eqs. (2.7) we straightforwardly obtain $A=-f^2/D_\perp$, $A_1=-f/D_\perp$, and $B=B_1=C=C_1=0$. Furthermore, only two scalar order parameters, $\langle F^2_{00}\rangle$ and $\langle F^4_{00}\rangle$, remain nonzero in the limit considered. [Note that the basis functions F^2_{00} and F^4_{00} are simply the second- and fourth-rank Legendre polynomials, respectively, $F^2_{00}(\boldsymbol{R})=P_2(\underline{\boldsymbol{n}}\cdot\boldsymbol{n})$, $F^4_{00}(\boldsymbol{R})=P_4(\underline{\boldsymbol{n}}\cdot\boldsymbol{n})$].

In the limit considered, the tumbling parameters λ_l and λ_m become identical and are equal to the parameter λ,

$$\lambda=f\frac{16S_4+5S_2+14}{35S_2}. \tag{3.1}$$

The third parameter, λ_n, becomes undefined, which should take place when the system possesses cylindrical symmetry and the director $\underline{\boldsymbol{n}}$ is perpendicular to the plane of shear.

All the ''biaxial'' coefficients, β_i and μ_i vanish in the discussed limiting case while the six ''nematic'' viscosities $\alpha_i\equiv\alpha_i^u$ reduce to the following formulas (within the common factor $dk_BT/2D_\perp$):

$$\alpha_1^u=-2\,f^2S_4,\quad \alpha_2^u=-f(1+\lambda^{-1})S_2,$$

$$\alpha_3^u=-f(1-\lambda^{-1})S_2,$$

$$\alpha_4^u=2\,f^2(7-5S_2-2S_4)/35,$$

$$\alpha_5^u=f[f(3S_2+4S_4)/7+S_2],$$

$$\alpha_6^u=f[f(3S_2+4S_4)/7-S_2],$$

where $S_2=\langle F^2_{00}\rangle$, $S_4=\langle F^2_{00}\rangle$.

The formulas quoted above for the Leslie viscosities are identical to those derived by Archer and Larson [14,15] and by Kröger and Sellers [16] for the uniaxial case. It should also be noted here that expression (3.1) for the tumbling parameter was obtained earlier by Stepanov [17]. Very similar formulas for the viscosity coefficients were also derived by Kuzuu and Doi [3]. The only difference between the Kuzuu-Doi results and ours concerns the tumbling parameter λ. In their paper [3], a complicated perturbation analysis was performed and a more accurate expression for λ, depending on the scalar order parameters as well as the mean-field potential, was obtained. However, the tumbling parameter calculated from the formula (3.1), obtained by neglecting flow-induced distortions of the scalar order parameters, is in excellent agreement with the experimental measurements for most of the known nematic liquid crystals [15].

When the uniaxial system is formed by biaxial molecules, the problem gets slightly more complicated. Some attention should be devoted to the parameters λ_l and λ_m, which remain different in the limit considered. They are given by the following formula:

$$\lambda_{l,m}=f_{l,m}\frac{3(16S_4+5S_2+14\mp5\sqrt{3}\langle F^2_{02}\rangle\pm8\,\sqrt{5}\langle F^4_{02}\rangle)}{35(3S_2\pm\sqrt{3}\langle F^2_{02}\rangle)},$$

where the upper and the lower signs correspond to the indices l and m, respectively. The two tumbling parameters quoted above represent two types of flow alignments which are possible in the case of a uniaxial system composed of biaxial molecules: λ_l and λ_m correspond to the situations in which the shear makes the molecules rotate around their short axes $\boldsymbol{m}$ and $\boldsymbol{l}$, respectively. Note also that parameter λ_n is, as in the previously discussed limiting case, undetermined.

Since there is only one tumbling parameter in the uniaxial phase, one of the quantities, either λ_l or λ_m, represents an alignment that is physically unreachable. Formally, in view of Eqs. (2.14)–(2.16), we have to set one of the multipliers, c_l or c_m, equal to zero, making the appropriate balance equation undetermined. Notice also that the condition $\lambda_l=\lambda_m$ reduces, in the limit considered, to the requirement $\gamma_3=0$. Unfortunately, within the approach presented we cannot establish which tumbling parameter describes the actual flow. One may, however, expect that it is the one that has the smaller magnitude, corresponding to the smaller value of the flow alignment angle.

The ''biaxial'' viscosities β_i and $\mu_{3,4}$ vanish after setting the biaxial parameters equal to zero. The viscosity μ_1 is given by $\mu_1=(\lambda_m^{-1}-\lambda_l^{-1})(C_1c_7+A_1d_1+B_1d_2)$. Thus, as $\lambda_l=\lambda_m$ in the limit considered, we also obtain that $\mu_1=\mu_2=0$.

The six ''uniaxial'' viscosities α_i, which remain nonvanishing, unfortunately cannot be written in such a compact form as in the case of axially symmetric molecules. They are still quite complex functions of the form factors, diffusion constants, and the five nematic order parameters.

An interesting feature of the derived formula α_i is the existence, apart from terms proportional to $1/D_l$ and $1/D_m$, of terms proportional to $1/D_n$. The latter are present even if one retains only the main order parameters $\langle F^2_{00}\rangle$ and $\langle F^4_{00}\rangle$. For example, after dropping the secondary order parameters, the viscosity coefficient α_1 reads (within the factor $dk_BT/2$)

$$\alpha_1=-\left[\left(\frac{f_m^2}{D_m}+\frac{f_l^2}{D_l}\right)-\frac{f_n^2}{4D_n}\right]\langle F^4_{00}\rangle.$$

Therefore, the ratios $D_{l,m}/D_n$ can serve as control parameters providing information as to whether the degree of freedom related to the rotation around the long molecular axis may by neglected while considering the viscosity of the uniaxial nematic liquid crystal.

The coefficients α_i^u describe the viscous properties of an idealized system composed of long, thin rods in which the diffusion constants D_l and D_m as well as the form factors f_l and f_m are identical. Moreover, not all effects related to the rotational motion about the long axis are taken into account. On the other hand, molecules composing real uniaxial nematics exhibit residual biaxiality in their shapes and in the diffusion coefficients as well. It is thus worth improving the formulas α_i^u so that the above-mentioned effects related to molecular anisotropy are taken into account. We show that the exact formulas (2.17) enable one to estimate the corrections to the viscosities α_i^u caused by the biaxiality of the molecules.

In the case of an elongated molecule, the constants D_l and D_m do not differ much, while the third diffusion constant is of considerably greater magnitude, $D_n \gg D_{l,m}$. It is thus convenient to describe the anisotropy of the diffusion coefficients and, thereby, to express the appropriate biaxial corrections in terms of two parameters δ and ϵ_1,

$$\delta = D_\perp / D_n, \tag{3.2}$$

$$\epsilon_1 = (D_l - D_m)/D_\perp, \tag{3.3}$$

with $D_\perp \equiv D_m$. Furthermore, to describe the anisotropy related to the form factors f_m and f_m we introduce the parameter ϵ_2,

$$\epsilon_2 = (f_l - f_m)/f, \tag{3.4}$$

where $f \equiv f_m$.

The parameter δ is the ratio between spinning and tumbling diffusion of the molecule. When it is small, all the terms proportional to $1/D_n$ may be neglected. The second parameter, ϵ_1, measures asymmetry in the rotational motion about the short axes. NMR studies of 4-methoxybenzylidene-4′-butylaniline (MBBA) [18,19] and 4-n-pentyloxybenzylidene-4′-heptylaniline (50.7) [20] show that δ is a quantity of the order of 10^{-2}. On the other hand, the experimental data of 50.7 [20] suggest that ϵ_1 may be of the order of 10^{-1}. One may thus assume that for a typical nematic liquid crystal composed of elongated molecules, $\epsilon_1 \gg \delta$. As far as the parameter ϵ_2 is concerned, no experimental evidence is available. Therefore, we assume that ϵ_1 and ϵ_2 are of the same order of magnitude. Hence, we will neglect in our considerations the parameter δ and express the corrections in terms of the parameters ϵ_1 and ϵ_2 only. Likewise, we neglect the secondary order parameters $\langle F_{ij}^l \rangle$, with $i \neq j$, since they are expected to be much smaller than S_2 and S_4 when the uniaxial system is composed of elongated molecules.

To calculate the corrections we express the diffusion coefficients and f_l and f_m, using the parameters $D_\perp$, δ, and ϵ_1, and f and ϵ_2, respectively, and insert them into Eq. (2.17). Next, we expand the appropriate formulas into series with respect to $\epsilon_{1,2}$ and δ, retaining only terms linear in ϵ_1 and ϵ_2. As a result we obtain

$$\alpha_{1,4} = \alpha_{1,4}^u (1 + 2\epsilon_a),$$

$$\alpha_{2,3} = \alpha_{2,3}^u (1 + 2\epsilon_b),$$

$$\alpha_{5,6} = \alpha_{5,6}^u + (\alpha_5^u + \alpha_6^u)\epsilon_a \mp \gamma_2^u \epsilon_b,$$

where $4\epsilon_a = 2\epsilon_2 - \epsilon_1$, $4\epsilon_b = \epsilon_1 - \epsilon_2$, and $\gamma_2^u = \alpha_6^u - \alpha_5^u$. In the last line, the signs "$-$" and "$+$" correspond to α_5 and α_6, respectively. Note also that the coefficients α_i quoted above obey the Onsager-Parodi relation $\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5$. The quantities ϵ_a and ϵ_b should be regarded as adjustable parameters that need to be evaluated by fitting to experimental data.

To complete this section, we must mention some facts concerning the three balance equations (2.14)–(2.16) in the limit of the $D_{\infty h}$ symmetry. It is easy to check that the first and third equations take the forms $\boldsymbol{g} \cdot \underline{\boldsymbol{l}} = 0$ and $\boldsymbol{g} \cdot \underline{\boldsymbol{m}} = 0$, respectively, where $\boldsymbol{g} = \gamma_2 \boldsymbol{A} \cdot \underline{\boldsymbol{n}} + \gamma_1 \boldsymbol{N}$. One may also prove that the second balance equation, Eq. (2.15), becomes undetermined in the limit discussed. We can rewrite both scalar equations obtained in an equivalent form as $\underline{\boldsymbol{n}} \times \boldsymbol{g} = \boldsymbol{0}$. We see, therefore, that in the limit of uniaxial symmetry Eqs. (2.14)–(2.16) recover the phenomenological equation for balance of angular momentum obtained by Ericksen and Leslie. Note here that the Ericksen-Leslie equation involves, in general, also the molecular field $\boldsymbol{h}$ and has the form $\underline{\boldsymbol{n}} \times (\boldsymbol{h} + \boldsymbol{g}) = \boldsymbol{0}$. However, at equilibrium, in the absence of external fields, the vector $\boldsymbol{h}$ is collinear to the director $\underline{\boldsymbol{n}}$ and may be omitted.

IV. THE ROTATIONAL DIFFUSION COEFFICIENTS

The formulas (2.17) derived in the preceding section allow one to predict all the Leslie viscosities, provided the axis ratio $a:b:c$ is established and the order parameters $\langle F_{ij}^l \rangle$ as well as the three rotational diffusion coefficients D_l, D_m, and D_n are known functions of temperature. All the above-mentioned quantities are, unfortunately, out of reach within the method we use to derive formulas for the viscosity coefficients; here they play the role of input parameters and must be calculated separately or taken from experiment.

However, the problem of the evaluation of the rotational diffusion tensor gets somewhat easier if one assumes that the molecule may be treated as a macroscopic body immersed in a viscous medium. Within this approximation, all the diffusion coefficients may be calculated by hydrodynamic methods. Such a treatment enables one to express the temperature dependences of D_l, D_m, and D_n, through the common medium viscosity η.

In order to determine the diffusion coefficients, we consider the selected molecule undergoing a stochastic rotational Brownian motion. Since the molecule is regarded as a macroscopic particle immersed in a viscous fluid, its rotational motion may be considered as rotational diffusion. Therefore, one can follow the Einstein concept and reduce the problem of calculating the diffusion coefficients to the problem of calculating the rotational friction coefficients, ξ_i $(i = l,m,n)$, which are defined in the molecular frame of reference by the relation $T_i = \xi_i \omega_i$, where $\boldsymbol{T}$ stands for the torque exerted on the molecule rotating with the angular velocity $\boldsymbol{\omega}$. The desired relation between ξ_i and D_i reads [21,22]

$$D_i = k_B T / \xi_i. \tag{4.1}$$

In our approach, the shapes of the molecules are modeled by ellipsoids with the principal axes **a**, **b**, **c**. The principal axes coincide with the molecular frame of reference, described by the unit vectors **l**, **m**, **n**, respectively. The most complete treatment of the problem of rotational motion of an ellipsoidal body immersed in a viscous medium was given long ago by Jeffery in Ref. [8]. According to Jeffery, components of the torque **T** acting on the particle rotating with a small angular velocity $\boldsymbol{\omega}$ are the following:

$$T_l = \frac{16\pi\eta}{3(b^2\beta_0 + c^2\gamma_0)}(b^2+c^2)\omega_l, \tag{4.2}$$

$$T_m = \frac{16\pi\eta}{3(c^2\gamma_0 + a^2\alpha_0)}(c^2+a^2)\omega_m, \tag{4.3}$$

$$T_n = \frac{16\pi\eta}{3(a^2\alpha_0 + b^2\beta_0)}(a^2+b^2)\omega_n, \tag{4.4}$$

where the constants α_0, β_0, and γ_0 are defined in Appendix C and $\eta = \eta(T)$ is the viscosity of the medium in which the molecule is immersed. Note that the lengths of the principal axes of the molecule considered are $2a$, $2b$, and $2c$, respectively.

From the relation (4.1) and Eqs. (4.2)–(4.4), we straightforwardly find

$$D_l = D_0\rho_l, \quad D_m = D_0\rho_m, \quad D_n = D_0\rho_n, \tag{4.5}$$

with

$$D_0 = 3k_BT/16\pi\eta, \tag{4.6}$$

and

$$\rho_l = \frac{b^2\beta_0 + c^2\gamma_0}{b^2+c^2}, \quad \rho_m = \frac{c^2\gamma_0 + a^2\alpha_0}{c^2+a^2}, \quad \rho_n = \frac{a^2\alpha_0 + b^2\beta_0}{a^2+b^2}. \tag{4.7}$$

Notice also that if the considered molecule is spherically symmetric $(a=b=c)$, Eqs. (4.5) reduce to the well-known Stokes formula

$$D_l = D_m = D_n = k_BT/8\pi\eta a^3.$$

Although the use of the formulas (4.5) yields a significant simplification of the problem of calculating the tensor D_{ij}, one should be aware that the applicability of the obtained expressions for the diffusion coefficients is, unfortunately, limited. The validity of the hydrodynamic approach that we have applied is, in general, not obvious; it is suitable only for description of the rotational diffusion of large molecules. In particular, the prediction that the $D_l:D_m:D_n$ ratio is independent of the temperature seems to be rather a rough approximation.

In the case of uniaxial nematics, the problem of rotational Brownian motion has been successfully described in the framework of the rotational diffusion model proposed by Tarroni and Zannoni [23], who have extended the Norido [24,25] model to asymmetric molecules. Within the Tarroni-Zannoni model, the temperature dependences of the rotational diffusion coefficients obey the simple Arrhenius rule, $D_i = D_0^i \exp[-E_a^i/k_BT]$, $i = l,m,n$, where E_a^i are activation energies and D_0^i are certain constants. The activation energies E_a^l and E_a^m characterizing the rotational motion around the short molecular axes are assumed to be identical, $E_a^l = E_a^m = E_a^\perp$. Such a treatment has proved to give a fairly good prediction of the temperature behavior of the diffusion coefficients in the case of nematic phases as well as smectic-A phases [20,26].

One can also expect that in the case of biaxial nematic phase, the temperature dependences of D_i are described by the Arrhenius-type relation with two different values of E_a^l and E_a^m. Therefore, the formulas (4.5) may be regarded as a rough approximation of the Tarroni-Zannoni model, in which all the activation energies are identical. One may also expect that Eqs. (4.5) give a good qualitative description of the temperature behavior of the diffusion coefficients, especially if one takes into account the fact that the diffusion coefficients vary rather smoothly with the temperature.

The use of the formulas (4.5) enables one to calculate relative magnitudes of the diffusion coefficients on the basis of the temperature dependences of the order parameters $\langle F_{ij}^l \rangle$ only. This is an important argument motivating analysis of the problem of the rotational diffusion tensor within the hydrodynamic approximation. In the next section we apply the derived formulas for the viscosity coefficients to a simple mean-field model of a biaxial nematic liquid crystal.

V. SAMPLE CALCULATIONS

To estimate the temperature behavior of relative magnitudes of the viscosity coefficients, we perform numerical calculations for a simple model of the biaxial phase, in which interactions between the molecular pairs are described by the modified Lennard-Jones potential [27]

$$U_{12} = U_{12}(\sigma/r) = 4\epsilon_0[(\sigma/r)^m - (\sigma/r)^n]. \tag{5.1}$$

Here $r = |\mathbf{r}|$ is the distance between the centers of mass of the molecules, parameter ϵ_0 is the depth of the potential, and σ is a scalar function depending on the orientations of the molecules, R_1 and R_2, and on the orientation R_u of the unit vector $\mathbf{u} \equiv \mathbf{r}/r$, $\sigma = \sigma(R_1, R_2, R_u)$. We use a relatively simple form of σ,

$$\begin{aligned}\sigma = {} & s_0 + s_1 F_{00}^2(R_2^{-1}R_1) + s_2 F_{22}^2(R_2^{-1}R_1) + s_3[F_{02}^2(R_2^{-1}R_1) \\ & + F_{20}^2(R_2^{-1}R_1)] + s_4[F_{00}^2(R_u^{-1}R_1) + F_{00}^2(R_u^{-1}R_2)] \\ & + s_5[F_{02}^2(R_u^{-1}R_1) + F_{02}^2(R_u^{-1}R_2)],\end{aligned} \tag{5.2}$$

where F_{ij}^l are invariants of the D_{2h} group defined in Appendix A, s_i are certain constants, and $R_2^{-1}R_1$ denotes the relative orientation of the molecular pair; $R_u^{-1}R_i$ $(i=1,2)$ stands for the relative orientation of the vector $\mathbf{u}$ and the ith molecule.

In order to determine the coefficients s_i, we assume that the molecules are modeled by ellipsoids with the principal axes $2a$, $2b$, and $2c$ and apply the modified excluded volume method [12]. It is assumed that for a fixed orientation of two molecules, a minimum distance between their centers of mass is determined by the condition $U_{12} = 0$. Such a treatment is a generalization of the method developed by Ruijgrok and Sokalski [27] in the case of nematic molecules. As a result, we obtain $s_0 = 2(a+b+c)/3$, $s_4 = (2c-b-a)/3$, $s_5 = \sqrt{3}(a-b)/3b$, and $s_1 = s_2 = s_3 = 0$.

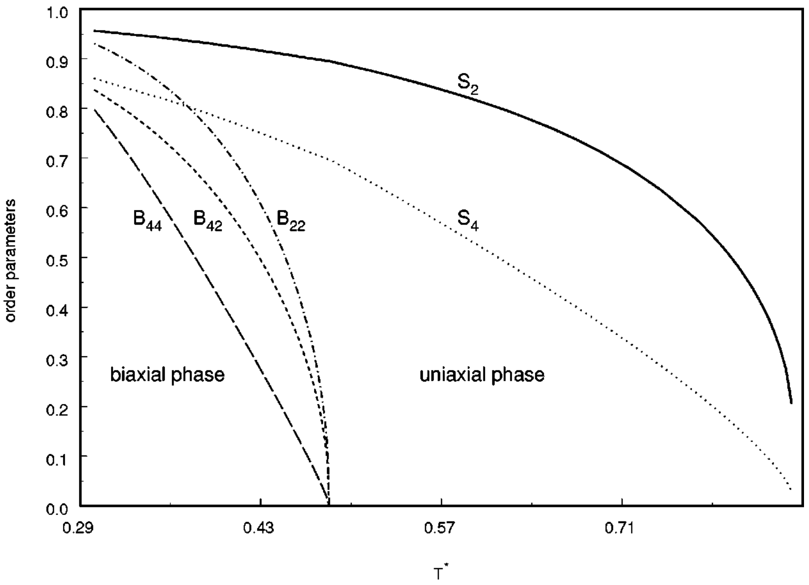

FIG. 1. Temperature dependence of the order parameters $S_2 = \langle F^2_{00} \rangle$, $S_4 = \langle F^4_{00} \rangle$, $B_{22} = \langle F^2_{22} \rangle$, $B_{42} = \langle F^4_{22} \rangle$, and, $B_{44} = \langle F^4_{44} \rangle$ on the reduced temperature $T^\star$.

Our aim is to find the one-particle distribution function F as a function of the temperature and, thereby, to determine the temperature dependence of the order parameters. For this purpose we follow the method proposed in Ref. [12]. It is based on the analysis of the Helmholtz free energy functional constructed within the Onsager [28] mean-field approximation. In the cited paper [12] we showed that the requirement that at equilibrium the free energy must be a minimum with respect to F leads to the following self-consistent equation of the Hammerstein type for the one-particle distribution function F:

$$\ln[F] = \lambda_0 \sum_{j=0,2} \sum_{\rho\mu\nu} K^j_{\rho\nu} F^j_{\mu\nu} \langle F^j_{\mu\rho} \rangle. \tag{5.3}$$

The parameter λ_0 is given by

$$\lambda_0 = \lambda_0(T^\star) = B_2(T^\star)\rho^\star / v_0, \tag{5.4}$$

where $T^\star = k_B T/\epsilon_0$ denotes a reduced temperature, $v_0 = 4\pi abc/3$ is the volume of the molecule, and $\rho^\star \equiv v_0 d$, with d being the number density, is the packing fraction. The function $B_2(T^\star)$ is given by the integral

$$B_2(T^\star) = \int_0^\infty x^2 \{\exp[-U_{12}(x)/k_B T] - 1\} dx.$$

For the Lennard-Jones potential, the above integral is expressed by the following infinite series:

$$3B_2(T^\star) = \sum_{s=0}^{\infty} \frac{1}{s!} \frac{n}{m} \left(\frac{1}{T^\star} \right)^{[(s+1)(m-n)+3]/m} \Gamma\left(\frac{sn+n-3}{m} \right) - \sum_{s=0}^{\infty} \frac{1}{s!} \left(\frac{1}{T^\star} \right)^{[s(m-n)+3]/m} \Gamma\left(\frac{sn+m-3}{m} \right). \tag{5.5}$$

The coefficients K^l_{ij} are the following analytical functions of the parameters s_i (within the common factor $4\pi/35$):

$$K^0_{00} = 35 s_0^3 + 42 s_5^2 s_0 - 12 s_5^2 s_4 + 42 s_4^2 s_0 + 4 s_4^3,$$

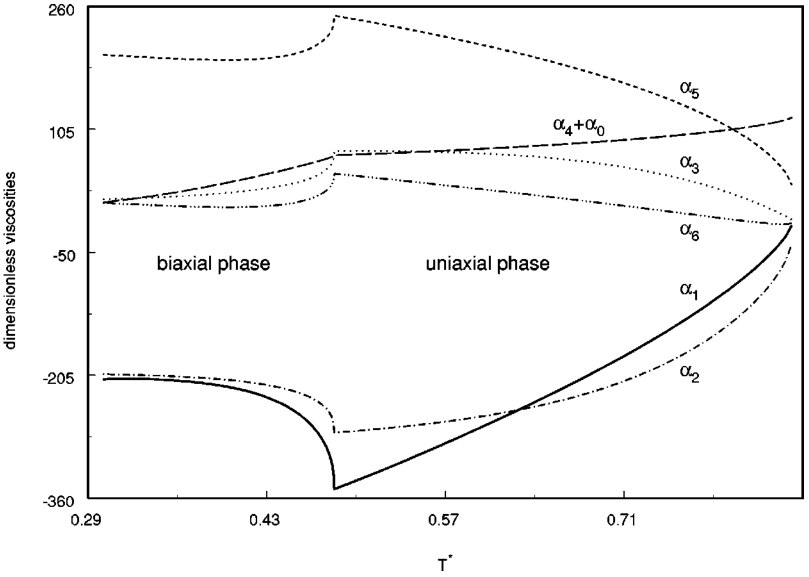

FIG. 2. Temperature dependence of the viscosity coefficients α_i on the reduced temperature $T^\star$. The results are given in units of $dk_B T/2D_0$.

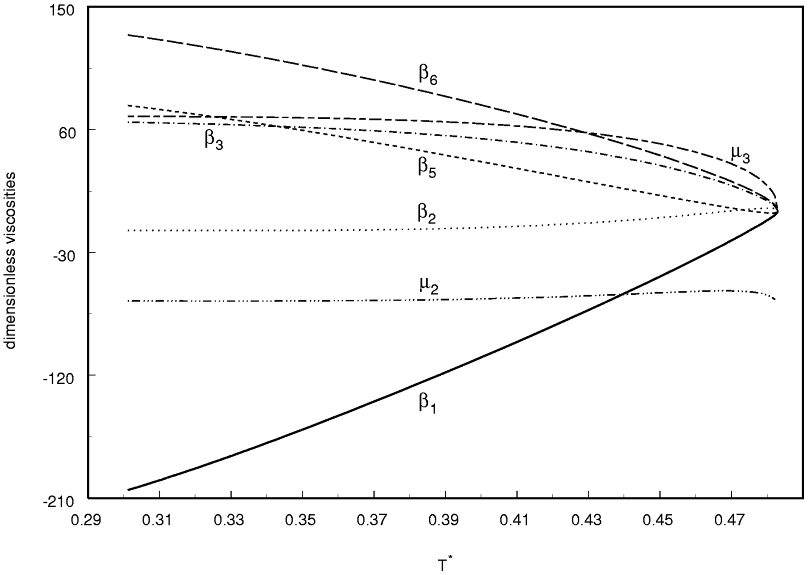

FIG. 3. Temperature dependence of the viscosity coefficients β_i and μ_i on the reduced temperature $T^\star$. The results are given in units of $dk_BT/2D_0$.

$$K_{00}^2=6s_4(2s_4^2+7s_4s_0-2s_5^2),$$

$$K_{20}^2=K_{02}^2=6s_5(7s_4s_0-s_4^2-s_5^2),$$

$$K_{22}^2=6s_5^2(7s_0-4s_4).$$

We have carried out the calculations for the Lennard-Jones potential (5.1) with $m=12$ and $n=6$ and for the ellipsoidal axis ratio $a:b:c=5:1:10$. For the assumed axis ratio, the form factors, f_l, f_m, and f_n are $f_l=-0.980$, $f_m=-0.600$, $f_n=0.923$. Likewise, the ratio of the rotational diffusion coefficients, according to Eq. (4.5), has been found to be $D_l:D_m:D_n=2.469:2.909:6.852$. The packing fraction $\rho^\star$ has been set equal to 0.2.

We have solved the self-consistent equation (5.3) numerically and calculated the thirteen order parameters $\langle F_{ij}^l\rangle$, $(l=2,4)$ as functions of the reduced temperature $T^\star$. In Fig. 1 the temperature dependences of the five main second- and fourth-rank order parameters, $\langle F_{00}^2\rangle$, $\langle F_{22}^2\rangle$, $\langle F_{00}^4\rangle$, $\langle F_{44}^4\rangle$, and $\langle F_{22}^4\rangle$ are plotted. It is also worth noting that the values of the remaining eight order parameters, $\langle F_{ij}^l\rangle$ with $i\neq j$, are two or three orders of magnitude smaller than those with $i=j$.

The values of the order parameters $\langle F_{ii}^l\rangle$ allow one to determine the phase uniquely. As seen, the system exhibits the first-order phase transition from isotropic to uniaxial nematic phase at $T^\star=0.841$ and the second-order phase transition from uniaxial to biaxial nematic phase at $T^\star=0.483$.

The obtained values of the order parameters allow us to calculate all the viscosities up to the common factor $dk_BT/2D_0$, which remains undetermined. However, this is enough to compare relative magnitudes of the viscosity coefficients.

At this point, one remark concerning the ''isotropic'' viscosity coefficient α_4 is in order. One should be aware that the formula derived describes the contribution to the viscosity originating only from the rotational motion of the molecules. In particular, it vanishes when the molecules are spherically symmetric. Thus, to take into account other contributions to momentum transport also, one has to modify the original viscosity α_4. The simplest way to improve α_4 is to replace it with the sum $\alpha_4+\alpha_0$ [15], where $\alpha_0=\alpha_0(T)$ is a certain viscosity coefficient that does not depend on the order parameters. In general, the new term, α_0, is a quantity whose temperature dependence needs to be taken from experiment. Fortunately, in this paper, to evaluate the viscosity α_0 we may make use of the fact that, within the hydrodynamic approximation, the coefficient α_4 and the shear viscosity η become identical in the isotropic phase. Therefore, the viscosity α_0 is given by the equation $\alpha_0=\eta-\alpha_4(\langle F_{ij}^l\rangle=0)$. Making use of the the relation (4.6), we easily find that, in units of $dk_BT/2D_0$, the viscosity α_0 is a constant

$$\alpha_0=\frac{3v_0}{8\pi\rho^\star}-\frac{1}{5}\left(\frac{f_l^2}{\rho_l}+\frac{f_m^2}{\rho_m}+\frac{f_n^2}{\rho_n}\right), \tag{5.6}$$

where the parameters ρ_i are given by Eqs. (4.7). We have also made use of the fact that, in the considered model of biaxial nematic, the packing fraction $\rho^\star$ and the number density d are linked by the relation $\rho^\star=dv_0$.

Figures 2 and 3 show the temperature behavior of the viscosities α_i, and β_i and μ_i, respectively. All the viscosity coefficients are given in units of $dk_BT/2D_0$, where $D_0=D_0(T)$ is given by Eq. (4.6). (To calculate the viscosities all thirteen order parameters have been used; in Fig. 1 only five of them are plotted.)

In the uniaxial phase, only the six uniaxial viscosities α_i are present. As seen, the coefficients α_1, α_5, and α_2 are of the greatest magnitudes, while the viscosity α_3 is negligible. It is also worth noting that the signs and relative magnitudes of the obtained viscosities close to the isotropic-nematic transition point are in fairly good agreement with the experimental evidence for MBBA [29]. One may thus expect that, in spite of all the approximations made, the results obtained capture the essential viscous properties of the biaxial phase.

Below the uniaxial-biaxial transition temperature, all fifteen viscosity coefficients are nonzero. In the deep biaxial phase one may divide them roughly, with respect to their magnitudes, into three groups. The four coefficients α_1, α_2, α_5, and β_1, are of the greatest magnitudes. Then, the seven viscosities β_3, β_5, β_6, $\mu_{1,2}$, and $\mu_{3,4}$, belong to the second group. Finally, the four viscosities α_3, α_4, α_6, and β_2 are, approximately, an order of magnitude smaller than those from the first group.

Magnitudes of the coefficients β_i and $\mu_{3,4}$ are, in units of $dk_BT/2D_0$, decreasing functions of temperature. Magnitudes of $\mu_{1,2}$ first decrease and then increase with temperature. As far as the viscosities α_1, α_2, α_3, α_5, and α_6 are concerned, their magnitudes increase with $T^\star$ in the biaxial phase and decrease after reaching the biaxial-uniaxial transition temperature. The coefficient α_4 is an increasing function of the temperature either in biaxial or in nematic phase.

Note also that the results obtained for the biaxial phase are, generally, in agreement with the predictions from Ref. [4]. In particular, they fulfill two inequalities that must be obeyed for a ''rodlike'' biaxial nematic: $\mu_1 > \mu_2$, and $\mu_1 - \mu_2 > \beta_3 - \beta_2$. Also, our results confirm the prediction that the viscosities μ_i cannot be small compared to the coefficients β_i.

According to Leslie, Laverty, and Carlsson [5], the requirement that the Rayleigh dissipation function has to be positively defined yields twelve inequalities for the viscosity coefficients to obey. They are quoted in Appendix D. It turns out that the obtained viscosities satisfy all the above-mentioned inequalities. However, one should be aware that the coefficients β_i are quite sensitive to the diffusion constants as well as the form factors and for certain values of $D_{l,m}$ and $f_{l,m}$ some of the inequalities may be not fulfilled. Nevertheless, the fact that the calculated viscosities obey the relations from Appendix D is very encouraging and testifies that the the proposed formulas (2.17) may be suited to describing the viscous properties of the biaxial phase.

VI. CONCLUSIONS

To summarize, in the present paper we have improved the method of deriving the Leslie viscosity coefficients for biaxial nematic liquid crystals presented in Ref. [1]. We have carried out all the calculations without using the decoupling procedures employed previously. The formulas obtained for the Leslie viscosities are expressed in terms of second- and fourth-rank order parameters, three rotational diffusion constants, number density, temperature, and certain parameters depending on the geometry of the molecules. What is important is that the viscosity coefficients presented satisfy the four Onsager-Parodi thermodynamical relations (2.2).

The method developed is based upon a relatively small number of assumptions, which makes our result quite general. In particular, the applicability of the viscosities derived is not limited by the use of a certain type of pair-interaction potential. The main assumption made, however, concerns the molecular shapes modeled by ellipsoids.

To our knowledge, pertinent formulas for the Leslie coefficients in the case of the biaxial system have not been presented before. Thus, in order to find a relation between our method and existing approaches we have investigated the obtained expressions in the limit of uniaxial symmetry. It turned out that in the limit considered, our results reproduce those obtained by Archer and Larson [15] and Kröger and Sellers [16] for the uniaxial system.

Furthermore, we have shown that it is possible to improve the above-mentioned limiting uniaxial formulas for the Leslie viscosities in such a way that the residual molecular biaxiality, related to the shape as well as the diffusion coefficients, is taken into account. We have found that in the case of uniaxial nematic liquid crystals composed of elongated molecules, all the effects due to the molecular biaxiality may be described by two parameters, ϵ_a and ϵ_b, which may be useful in interpreting experimental data.

In the present paper we have also dealt with the issue of the diffusion coefficients D_l, D_m, and D_n. We have considered the stochastic rotational motion of the molecules within the hydrodynamic approximation and expressed the temperature dependence of the diffusion coefficients through the common shear viscosity η. This enabled us to estimate the relative magnitudes of the viscosity coefficients. We have carried out the appropriate calculations for a simple model of a biaxial nematic liquid crystal in which the pair interactions are described by the modified Lennard-Jones potential. We have found that in the biaxial phase, near the uniaxial-biaxial transition point, magnitudes of the biaxial viscosities β_i and μ_i are much smaller than the magnitudes of the largest uniaxial coefficients α_2, α_5, and α_1. However, in the deep biaxial phase, the coefficients β_i have proved to be of the same order of magnitude as the viscosities α_i.

VII. ACKNOWLEDGMENT

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APPENDIX A

The basic functions F^l_{ij} generating the solution space for the biaxial system are given by the following formula [12,30]:

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

where l,i,j are integer numbers and $\boldsymbol{R}$ is the rotation parameterized by three Euler angles. $D^{(l)}_{ij}$ are the standard rotation matrix elements. The functions F^l_{ij} obey the orthonormality relation

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

APPENDIX B

The calculated coefficients a_i, b_i, c_i, and d_i are as follows:

$$a_1=\langle F^4_{00}\rangle-2\,\frac{\sqrt{5}}{5}\langle F^4_{20}\rangle+\frac{\sqrt{35}}{35}\langle F^4_{40}\rangle,\quad a_2=8\,\frac{\sqrt{35}}{35}\langle F^4_{40}\rangle,$$

$$a_3=\frac{2}{15}-\frac{4}{21}\langle F^2_{00}\rangle+4\,\frac{\sqrt{3}}{21}\langle F^2_{20}\rangle+\frac{2}{35}\langle F^4_{00}\rangle-6\,\frac{\sqrt{5}}{35}\langle F^4_{20}\rangle+2\,\frac{\sqrt{35}}{35}\langle F^4_{40}\rangle,$$

$$a_4=-\frac{1}{15}+\frac{2}{21}\langle F^2_{00}\rangle-2\,\frac{\sqrt{3}}{21}\langle F^2_{20}\rangle-\frac{1}{35}\langle F^4_{00}\rangle-4\,\frac{\sqrt{5}}{35}\langle F^4_{20}\rangle+\frac{\sqrt{35}}{35}\langle F^4_{40}\rangle,$$

$$a_5=\frac{2}{15}+\frac{2}{21}\langle F^2_{00}\rangle+2\,\frac{\sqrt{3}}{21}\langle F^2_{20}\rangle-\frac{8}{35}\langle F^4_{00}\rangle+4\,\frac{\sqrt{5}}{35}\langle F^4_{20}\rangle,$$

$$a_6=\frac{2}{15}-\frac{4}{21}\langle F^2_{00}\rangle+\frac{2}{35}\langle F^4_{00}\rangle-2\,\frac{\sqrt{35}}{35}\langle F^4_{40}\rangle,$$

$$b_1=\frac{3}{8}\langle F^4_{00}\rangle+\frac{\sqrt{5}}{4}\langle F^4_{02}\rangle+\frac{\sqrt{35}}{8}\langle F^4_{04}\rangle-3\,\frac{\sqrt{5}}{20}\langle F^4_{20}\rangle-\frac{1}{2}\langle F^4_{22}\rangle-\frac{\sqrt{7}}{4}\langle F^4_{24}\rangle+3\,\frac{\sqrt{35}}{280}\langle F^4_{40}\rangle+\frac{\sqrt{7}}{28}\langle F^4_{42}\rangle+\frac{1}{8}\langle F^4_{44}\rangle,$$

$$b_2=3\,\frac{\sqrt{35}}{35}\langle F^4_{40}\rangle+2\,\frac{\sqrt{7}}{7}\langle F^4_{42}\rangle+\langle F^4_{44}\rangle,$$

$$b_3=\frac{2}{15}+\frac{2}{21}\langle F^2_{00}\rangle+2\,\frac{\sqrt{3}}{21}\langle F^2_{02}\rangle-2\,\frac{\sqrt{3}}{21}\langle F^2_{20}\rangle-\frac{2}{7}\langle F^2_{22}\rangle+\frac{3}{140}\langle F^4_{00}\rangle+\frac{\sqrt{5}}{70}\langle F^4_{02}\rangle+\frac{\sqrt{35}}{140}\langle F^4_{04}\rangle-9\,\frac{\sqrt{5}}{140}\langle F^4_{20}\rangle-\frac{3}{14}\langle F^4_{22}\rangle$$
$$-3\,\frac{\sqrt{7}}{28}\langle F^4_{24}\rangle+3\,\frac{\sqrt{35}}{140}\langle F^4_{40}\rangle+\frac{\sqrt{7}}{14}\langle F^4_{42}\rangle+\frac{1}{4}\langle F^4_{44}\rangle,$$

$$b_4=-\frac{1}{15}-\frac{1}{21}\langle F^2_{00}\rangle-\frac{\sqrt{3}}{21}\langle F^2_{02}\rangle+\frac{\sqrt{3}}{21}\langle F^2_{20}\rangle+\frac{1}{7}\langle F^2_{22}\rangle-\frac{3}{280}\langle F^4_{00}\rangle-\frac{\sqrt{5}}{140}\langle F^4_{02}\rangle-\frac{\sqrt{35}}{280}\langle F^4_{04}\rangle-3\,\frac{\sqrt{5}}{70}\langle F^4_{20}\rangle-\frac{1}{7}\langle F^4_{22}\rangle-\frac{\sqrt{7}}{14}\langle F^4_{24}\rangle$$
$$+3\,\frac{\sqrt{35}}{280}\langle F^4_{40}\rangle+\frac{\sqrt{7}}{28}\langle F^4_{42}\rangle+\frac{1}{8}\langle F^4_{44}\rangle,$$

$$b_5=\frac{2}{15}-\frac{1}{21}\langle F^2_{00}\rangle-\frac{\sqrt{3}}{21}\langle F^2_{02}\rangle-\frac{\sqrt{3}}{21}\langle F^2_{20}\rangle-\frac{1}{7}\langle F^2_{22}\rangle-\frac{3}{35}\langle F^4_{00}\rangle-2\,\frac{\sqrt{5}}{35}\langle F^4_{02}\rangle-\frac{\sqrt{35}}{35}\langle F^4_{04}\rangle+3\,\frac{\sqrt{5}}{70}\langle F^4_{20}\rangle+\frac{1}{7}\langle F^4_{22}\rangle+\frac{\sqrt{7}}{14}\langle F^4_{24}\rangle,$$

$$b_6=\frac{2}{15}+\frac{2}{21}\langle F^2_{00}\rangle+2\,\frac{\sqrt{3}}{21}\langle F^2_{02}\rangle+\frac{3}{140}\langle F^4_{00}\rangle+\frac{\sqrt{5}}{70}\langle F^4_{02}\rangle+\frac{\sqrt{35}}{140}\langle F^4_{04}\rangle-3\,\frac{\sqrt{35}}{140}\langle F^4_{40}\rangle-\frac{\sqrt{7}}{14}\langle F^4_{42}\rangle-\frac{1}{4}\langle F^4_{44}\rangle,$$

$$c_1=-\frac{1}{2}\langle F^4_{00}\rangle-\frac{\sqrt{5}}{4}\langle F^4_{02}\rangle+\frac{\sqrt{5}}{5}\langle F^4_{20}\rangle+\frac{1}{2}\langle F^4_{22}\rangle-\frac{\sqrt{35}}{70}\langle F^4_{40}\rangle-\frac{\sqrt{7}}{28}\langle F^4_{42}\rangle,$$

$$c_2=-4\,\frac{\sqrt{35}}{35}\langle F^4_{40}\rangle-2\,\frac{\sqrt{7}}{7}\langle F^4_{42}\rangle,$$

$$c_3=\frac{1}{10}-\frac{1}{14}\langle F^2_{00}\rangle+\frac{\sqrt{3}}{14}\langle F^2_{02}\rangle+\frac{\sqrt{3}}{14}\langle F^2_{20}\rangle-\frac{3}{14}\langle F^2_{22}\rangle-\frac{1}{35}\langle F^4_{00}\rangle-\frac{\sqrt{5}}{70}\langle F^4_{02}\rangle+3\,\frac{\sqrt{5}}{35}\langle F^4_{20}\rangle+\frac{3}{14}\langle F^4_{22}\rangle-\frac{\sqrt{35}}{35}\langle F^4_{40}\rangle-\frac{\sqrt{7}}{14}\langle F^4_{42}\rangle,$$

$$c_4=-\frac{1}{10}+\frac{1}{14}\langle F^2_{00}\rangle-\frac{\sqrt{3}}{14}\langle F^2_{02}\rangle-\frac{\sqrt{3}}{14}\langle F^2_{20}\rangle+\frac{3}{14}\langle F^2_{22}\rangle+\frac{1}{35}\langle F^4_{00}\rangle+\frac{\sqrt{5}}{70}\langle F^4_{02}\rangle+4\,\frac{\sqrt{5}}{35}\langle F^4_{20}\rangle+\frac{2}{7}\langle F^4_{22}\rangle-\frac{\sqrt{35}}{35}\langle F^4_{40}\rangle-\frac{\sqrt{7}}{14}\langle F^4_{42}\rangle,$$

$$c_5=\frac{1}{5}+\frac{1}{14}\langle F^2_{00}\rangle-\frac{\sqrt{3}}{14}\langle F^2_{02}\rangle+\frac{\sqrt{3}}{14}\langle F^2_{20}\rangle-\frac{3}{14}\langle F^2_{22}\rangle+\frac{8}{35}\langle F^4_{00}\rangle+4\,\frac{\sqrt{5}}{35}\langle F^4_{02}\rangle-4\,\frac{\sqrt{5}}{35}\langle F^4_{20}\rangle-\frac{2}{7}\langle F^4_{22}\rangle,$$

$$c_6=\frac{1}{5}-\frac{1}{7}\langle F^2_{00}\rangle+\frac{\sqrt{3}}{7}\langle F^2_{02}\rangle-\frac{2}{35}\langle F^4_{00}\rangle-\frac{\sqrt{5}}{35}\langle F^4_{02}\rangle+2\,\frac{\sqrt{35}}{35}\langle F^4_{40}\rangle+\frac{\sqrt{7}}{7}\langle F^4_{42}\rangle,$$

$$c_7=-\frac{1}{2}\langle F_{00}^2\rangle+\frac{\sqrt{3}}{6}\langle F_{20}^2\rangle-\frac{\sqrt{3}}{6}\langle F_{02}^2\rangle+\frac{1}{6}\langle F_{22}^2\rangle,$$

$$c_8=\frac{\sqrt{3}}{3}\langle F_{20}^2\rangle+\frac{1}{3}\langle F_{22}^2\rangle,$$

$$d_1=\langle F_{00}^2\rangle-\frac{\sqrt{3}}{3}\langle F_{20}^2\rangle,\quad d_2=-\frac{1}{2}\langle F_{00}^2\rangle-\frac{\sqrt{3}}{2}\langle F_{02}^2\rangle+\frac{\sqrt{3}}{6}\langle F_{20}^2\rangle+\frac{1}{2}\langle F_{22}^2\rangle,$$

$$d_3=\frac{\sqrt{3}}{3}\langle F_{20}^2\rangle+\langle F_{22}^2\rangle,\quad d_4=-\frac{2\sqrt{3}}{3}\langle F_{20}^2\rangle.$$

APPENDIX C

The parameters α_0, β_0, and γ_0 are given by the following integrals:

$$\alpha_0=a^{-3}\int_0^\infty (x+1)^{-3/2}[x+(b/a)^2]^{-1/2}[x+(c/a)^2]^{-1/2}dx,$$

$$\beta_0=b^{-3}\int_0^\infty (x+1)^{-3/2}[x+(a/b)^2]^{-1/2}[x+(c/b)^2]^{-1/2}dx,$$

$$\gamma_0=c^{-3}\int_0^\infty (x+1)^{-3/2}[x+(b/c)^2]^{-1/2}[x+(a/c)^2]^{-1/2}dx.$$

APPENDIX D

Due to the requirement that Rayleigh dissipation function must be positive, the viscosity coefficients have to obey the following twelve inequalities [5]:

$$2\alpha_4+\alpha_5+\alpha_6>0,\quad 2\alpha_4+\beta_5+\beta_6>0,$$

$$2\alpha_4+\alpha_5+\alpha_6+\beta_5+\beta_6+\mu_3+\mu_4>0,\quad 2\alpha_4+\alpha_5+\alpha_6+\alpha_1>0,$$

$$2\alpha_4+\beta_5+\beta_6+\beta_1>0,\quad \gamma_1>0,\quad \lambda_1>0,\quad \gamma_1+\lambda_1+\gamma_3>0,$$

$$\alpha_4^2<(2\alpha_4+\alpha_5+\alpha_6+\alpha_1)(2\alpha_4+\beta_5+\beta_6+\beta_1),$$

$$\gamma_2^2<\gamma_1(2\alpha_4+\alpha_5+\alpha_6),\quad \lambda_2^2<\lambda_1(2\alpha_4+\beta_5+\beta_6),$$

$$(\alpha_6-\alpha_5-\beta_6+\beta_5+\mu_4-\mu_3)^2>(\gamma_1+\lambda_1+\gamma_3)(2\alpha_4+\alpha_5+\alpha_6+\beta_5+\beta_6+\mu_3+\mu_4).$$

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