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Microscopic description of nematic liquid crystal viscosity

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The problem of nematic viscosity is shown to be successfully solved within the framework of a microscopic description. The Kuzuu-Doi approach to hydrodynamics [N. Kuzuu and M. Doi, J. Phys. Soc. Jpn. **52**, 3486 (1983)] for a system consisting of anisotropic molecules is reviewed. It has been shown that the incorrect form of the microscopic stress tensor that is used by Kuzuu and Doi does not influence final expressions for the viscosity coefficients due to the fact that the external magnetic field is taken into account. Molecular expressions for the Leslie viscosity coefficients are calculated by use of the theory of Osipov and Terentjev [Z. Naturforsch. Teil A **44**, 785 (1989); Phys. Lett. A **134**, 301 (1989)]. A systematic solution of the differential kinetic equation is presented. The nonequilibrium distribution function obtained from the kinetic equation allows us to transform Osipov-like expressions for the viscosity coefficients exactly into those obtained by Kuzuu and Doi. The above-mentioned approaches are proved to be equivalent. A realistic mean potential is applied to the expressions obtained for the Leslie coefficients for the case of 4-methoxybenzylidene-4′-*n*-butylaniline. A comparison of theoretical results and appropriate experimental data is shown to be very good.

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I. INTRODUCTION

Since the overwhelming majority of theoretical investigations into hydrodynamics of liquid crystals has been made on the basis of phenomenological equations, it seems to be reasonable to justify them by the use of appropriate statistical theories. Some attempts to create such theories have been undertaken so far, among which the pioneer theory of Diogo and Martins [1–3] is worth looking into. They start their consideration from the assumption that the viscosity coefficients of nematic liquid crystals are proportional to the characteristic relaxation time that is related to the probability of overcoming a potential barrier during molecular reorientation. Although Diogo and Martins have obtained *microscopic* expressions for the Leslie coefficients, their theory contains too many free parameters. Some attempts to provide an explanation of the exponential behavior of the viscosity coefficients can be found in papers [4–6].

In 1981 Doi [7] proposed an approach to elaborate a statistical theory of hydrodynamics of systems made of ellipsoidal molecules. This theory was improved in [8] by Kuzuu and Doi. They obtained microscopic expressions for the Leslie coefficients in terms of order parameters. Although their predictions were successful, the way in which they provided their analysis has some shortcomings, which could cast a shadow on the final outcome. Understanding these weak points allows us to answer whether or not the expressions for the Leslie coefficients obtained by Kuzuu and Doi are reliable.

Kuzuu and Doi focused their attention on the fact that the stress tensor is an average of its microscopic counterpart performed with an appropriate nonequilibrium distribution function. The point is that the expression for the microscopic stress tensor they used was not accurately derived and correctly gave only the symmetric part of it. Moreover, they treated the stress tensor as a completely symmetric object, which cannot be true, since the existence of the asymmetric part of it is one of the most typical features of liquid crystals. They offset that lack by introducing the influence of a magnetic field, which produces an asymmetric contribution to the microscopic viscosity stress tensor. On the whole, their analysis gave the impression that asymmetry of viscous properties of nematics is not possible without a magnetic field.

Next they noticed that the symmetric part of the stress tensor can be reconstructed from the kinetic equation multiplied by the tensor $Q_{\alpha\beta}$ without *de facto* solving it. Since the form of the symmetric microscopic stress tensor is correct, Doi's whole analysis of the symmetrical viscous stress tensor should be valid.

Kuzuu and Doi's analysis concerning asymmetry is based on a perturbative method of solving the kinetic equation, which in lowest order reconstructs the Leslie phenomenological constitutive equation containing asymmetric viscosity coefficients. From this equation it emerges that the contribution from the magnetic field to the viscous stress tensor can be replaced by appropriate terms with asymmetric coefficients γ_1 and γ_2. This part of Kuzuu and Doi's considerations does not require knowledge of the asymmetric microscopic stress tensor so, despite some misunderstandings, the final outcome of their theory is fully reliable.

Following the idea of Kuzuu-Doi of considering an average of the microscopic stress tensor with an appropriate nonequilibrium distribution function, Osipov and Terentjev suggested another approach [9,10]. The main point of their idea is the form of the distribution function. They have noticed that flow breaks the cylindrical symmetry of a nematic liquid crystal and suggested, within the assumption of low velocity gradients, that the nonequilibrium distribution function should consist of the equilibrium one and the contribution determined by the velocity gradients combined with the components of the director $\vec{n}$ and the azimuth dependent vector $\vec{e}$. This approach seems to be very reasonable and one should expect that both the Kuzuu-Doi (KD) and the Osipov-Terentjev (OT) theories should coincide. Nevertheless, such a result has not been arrived at so far.

The main purpose of this work is to show equivalence of the above-mentioned hydrodynamic theories, apply these theories to the particular case, and compare results to experimental data. In Sec. II the fundamental phenomenological equations governing viscosity of a nematic are recalled. In Sec. III the KD way of deriving the Leslie coefficients is reviewed. Section IV presents the microscopic expressions for the viscosity coefficients, which we have obtained in the OT approach, and then a systematic analysis of solutions of the kinetic equation. Section V shows that the KD and OT approaches lead to the same results as far as viscosity coefficients are concerned; in other words, both these approaches are equivalent. In Sec. VI a realistic mean potential for 4-methoxybenzylidene-4′-n-butylaniline (MBBA) is applied to the hydrodynamic theories. A comparison of theoretical results and experimental data is shown to be very satisfactory.

II. PHENOMENOLOGICAL HYDRODYNAMICS

Equations describing hydrodynamics are formulated as conservation laws for several suitable quantities related to the hydrodynamic variables. In the case of an incompressible, undeformed, nematic liquid crystal, the laws of interests are the equation of continuity, conservation of linear momentum, and the director equation [11–16].

The equation of continuity reads

$$\vec{\nabla} \cdot \vec{v} = 0, \tag{1}$$

where $\vec{v}$ is the velocity field. Conservation of linear momentum (Navier-Stokes equation) is

$$\rho \frac{dv_i}{dt} = -\Pi_i + \partial_j \sigma_{ji}, \tag{2}$$

where $\frac{dv_i}{dt} = \frac{\partial v_i}{\partial t} + \vec{v} \cdot \vec{\nabla}$, ρ is the density, $\Pi_i = \partial_j(p\delta_{ij})$ denotes the pressure term, and σ_{ij} is the viscous stress tensor. The viscous stress tensor due to the derivation of Leslie [12–14] reads

$$\begin{aligned}\sigma_{\alpha\beta} = {} & \alpha_1 n_\alpha n_\beta n_\rho n_\mu A_{\mu\rho} + \alpha_2 n_\alpha N_\beta + \alpha_3 n_\beta N_\alpha \\ & + \alpha_4 A_{\alpha\beta} + \alpha_5 n_\alpha n_\mu A_{\mu\beta} + \alpha_6 n_\beta n_\mu A_{\mu\alpha},\end{aligned} \tag{3}$$

where $A_{\alpha\beta} = (\partial_\alpha v_\beta + \partial_\beta v_\alpha)/2$ and $g^a_{\alpha\beta} = (\partial_\alpha v_\beta - \partial_\beta v_\alpha)/2$ are the symmetric and asymmetric parts of the velocity gradient field. The possible system rotations are reflected by the vector $N_\alpha = \dot{n}_\alpha - (\omega \times n)_\alpha$, where $\omega = \frac{1}{2}\mathrm{rot}\vec{v}$ is the flow rotation angular velocity. The viscosity constants $\alpha_1, \ldots, \alpha_6$ are called the Leslie coefficients and are typical for a nematic phase. In the isotropic phase all of them vanish except α_4, which becomes the isotropic shear viscosity coefficient. They have to fulfill the Onsager reciprocal relation, which for a nematic is known as the Parodi relation [17]

$$\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5 \; . \tag{4}$$

So, effectively, there are five independent coefficients. Three of them are connected with the symmetric part of the stress tensor and the other two with the asymmetric part

$$\begin{aligned}\sigma^{\mathrm{asym}}_{\alpha\beta} = {} & \frac{\gamma_1}{2}(n_\beta N_\alpha - n_\alpha N_\beta) \\ & + \frac{\gamma_2}{2}(n_\beta n_\mu A_{\mu\alpha} - n_\alpha n_\mu) A_{\mu\beta},\end{aligned} \tag{5}$$

where $\gamma_1 = \alpha_3 - \alpha_2$ and $\gamma_2 = \alpha_6 - \alpha_5$. Coefficients γ_1 and γ_2 determine the viscous torque acting on the molecule: γ_1 is characteristic for the torque associated with an angular velocity of the director and γ_2 for the contribution due to a shear velocity.

The third important equation in hydrodynamics of nematics is the director equation

$$0 = \vec{n} \times (\gamma_1 \vec{N} + \gamma_2 \vec{n} \mathbf{A}). \tag{6}$$

Within the assumption of undeformed director field ($\partial_\alpha n_\beta = 0$) the conservation law for angular momentum can be neglected. If one would like to consider the case of a deformed system, this conservation law should be taken into account and also one should extend Eqs. (6) and (2) to the general forms containing elasticity terms.

III. THE KUZUU-DOI APPROACH

A. Symmetric part of the stress tensor

In this section we review Doi's approach [7,8] which results in the concept of treating the stress tensor σ as an average of its microscopic equivalent σ^{micr} performed with an appropriate nonequilibrium distribution function. Under the assumption that microscopic molecular motion in a nematic liquid crystal can be considered as a rotational Brownian motion in an external mean potential, the following kinetic equation determines the nonequilibrium distribution function $f(\vec{a}, t)$ [7–10,18,19]:

$$\dot{f} + \epsilon \partial_k (f \Omega_k) = \epsilon^2 \partial_k \left(\partial_k f - \frac{\Gamma_k}{kT} f \right) , \tag{7}$$

where the differential operator $\partial_k = \epsilon_{kij} a_i \frac{\partial}{\partial a_j}$ describes an infinitesimal rotation of the long molecular axis $\vec{a}$ and $\Gamma_k = -\partial_k U(\vec{a} \cdot \vec{n})$ is the moment of force acting on the molecule in the mean potential U. Thus the first term on the right-hand side of (7) represents the rotational Brownian motion and the second is due to the rotation caused by the potential U. The second term on the left-hand side in (7) represents the effect of the velocity gradient, which rotates the molecule with a certain average angular velocity $\vec{\Omega}$. For an ellipsoidal molecule it has the form [20,21]

$$\vec{\Omega} = \frac{p^2-1}{p^2+1}\vec{a} \times (\mathbf{A} \cdot \vec{a}) - \vec{a} \times (\mathbf{g}^a \cdot \vec{a}) \ , \tag{8}$$

where $\frac{p^2-1}{p^2+1}$ is the form factor based on the length to width ratio p of the molecule. In (7) the small parameter $\epsilon = \frac{\tau_\omega}{\tau_a} \ll 1$ [9] is the ratio of two characteristic times of the system: the correlation time $\tau_\omega = J/\lambda$, where λ is the coefficient of internal friction and J the moment of inertia of the molecule, and the relaxation time $\tau_a = \sqrt{kT/J}$. On the other hand, ϵ can be treated as the rotational diffusion coefficient.

The idea of Kuzuu and Doi is to multiply the kinetic equation by the tensor $(a_\alpha a_\beta - \delta_{\alpha\beta}/3)$ and integrate over $\vec{a}$. Let us quote their results:

$$\frac{\partial Q_{\alpha\beta}}{\partial t} = F_{\alpha\beta} + G_{\alpha\beta}, \tag{9}$$

where

$$Q_{\alpha\beta} = \left\langle a_\alpha a_\beta - \frac{\delta_{\alpha\beta}}{3} \right\rangle, \tag{10}$$

$$F_{\alpha\beta} = -6\epsilon\left\langle a_\alpha a_\beta - \frac{\delta_{\alpha\beta}}{3} \right\rangle + \frac{\epsilon}{kT}\left\langle a_\alpha \frac{\partial U}{\partial a_\beta} + a_\beta \frac{\partial U}{\partial a_\alpha} \right\rangle \tag{11}$$

and

$$\begin{aligned} G_{\alpha\beta} = \frac{p^2-1}{p^2+1}&[A_{\alpha\mu}\langle a_\mu a_\beta\rangle + \langle a_\alpha a_\mu\rangle A_{\mu\beta} \\ &-2\langle a_\alpha a_\beta a_\gamma a_\mu\rangle A_{\gamma\mu}] - g_{\alpha\mu}\langle a_\mu a_\beta\rangle + \langle a_\alpha a_\mu\rangle g_{\mu\beta}. \end{aligned} \tag{12}$$

In (11) and (12) we have deliberately omitted parts containing the magnetic field as originally introduced by Kuzuu and Doi. We would like to show that their approach is valid either with or without magnetic field.

By the use of Doi's idea it has been shown [22] that σ^{micr} has the form

$$\begin{aligned} \sigma^{\text{micr}}_{\alpha\beta} = 3kT&\frac{p^2-1}{p^2+1}\left(a_\alpha a_\beta - \frac{\delta_{\alpha\beta}}{3}\right) \\ &+\left(\frac{p^2}{p^2+1}a_\alpha\frac{\partial U}{\partial a_\beta} - \frac{1}{p^2+1}a_\beta\frac{\partial U}{\partial a_\alpha}\right). \end{aligned} \tag{13}$$

From (11) and (12) it emerges that $F_{\alpha\beta}$ and $G_{\alpha\beta}$ relate to the symmetric stress tensor as

$$\sigma^{\text{sym}}_{\alpha\beta} = -\frac{kT}{2\epsilon}\frac{p^2-1}{p^2+1}F_{\alpha\beta} = \frac{kT}{2\epsilon}\frac{p^2-1}{p^2+1}\left(G_{\alpha\beta} - \frac{\partial Q_{\alpha\beta}}{\partial t}\right). \tag{14}$$

From (14) it emerges that it is possible to replace the expression for σ^{sym} with the nonequilibrium distribution function by the expression containing only the known equilibrium one. Since $G_{\alpha\beta}$ is already linearly dependent on velocity gradients $\partial_\alpha v_\beta$, the averages $\langle\,\rangle$ can be performed there with the known equilibrium distribution function. It means that to derive the symmetric Leslie coefficients practically only the expression for the angular velocity is needed. It is convenient to express σ^{sym} in terms of the two irreducible tensors Q_2 and Q_4. Equilibrium values of these order parameters have forms

$$Q_{2_{\alpha\beta}} = S_2\left\langle n_\alpha n_\beta - \frac{\delta_{\alpha\beta}}{3}\right\rangle, \tag{15}$$

$$\begin{aligned} Q_{4_{\alpha\beta\gamma\mu}} = S_4\langle n_\alpha n_\beta n_\gamma n_\mu &+ \frac{1}{35}(\delta_{\alpha\beta}\delta_{\gamma\mu} + \delta_{\alpha\gamma}\delta_{\beta\mu} + \delta_{\alpha\mu}\delta_{\gamma\beta}) \\ &-\frac{1}{7}(n_\alpha n_\beta\delta_{\gamma\mu} + n_\gamma n_\mu\delta_{\alpha\beta} + n_\alpha n_\gamma\delta_{\beta\mu} \\ &+n_\beta n_\mu\delta_{\alpha\gamma} + n_\alpha n_\mu\delta_{\gamma\beta} + n_\gamma n_\beta\delta_{\alpha\mu})\rangle, \end{aligned} \tag{16}$$

where $S_2 = \langle P_2\rangle$, $S_4 = \langle P_4\rangle$, and P_2, P_4 are the second- and fourth-order Legendre polynomials.

As a result we obtain

$$\begin{aligned} \sigma^{\text{sym}}_{\alpha\beta} = \frac{kT}{2\epsilon}\left[\frac{p^2-1}{p^2+1}\right]^2 &\Big[-2S_4(A_{\mu\rho}n_\mu n_\rho)n_\alpha n_\beta \\ &+\frac{2}{35}(7-5S_2-2S_4)A_{\alpha\beta} \\ &+\frac{1}{7}(3S_2+4S_4)(n_\alpha n_\mu A_{\mu\beta} + A_{\alpha\mu}n_\mu n_\beta)\Big] \\ &-\frac{kT}{2\epsilon}\frac{p^2-1}{p^2+1}S_2(g^a_{\alpha\mu}n_\mu n_\beta - n_\alpha n_\mu g^a_{\beta\mu}). \end{aligned} \tag{17}$$

Comparing (17) to the phenomenological form of the viscosity tensor (3), the following set of microscopic expressions for the symmetric Leslie coefficients is obtained:

$$\alpha_1 = -\frac{kT}{\epsilon}\left[\frac{p^2-1}{p^2+1}\right]^2 S_4, \tag{18}$$

$$\alpha_2 + \alpha_3 = -\frac{kT}{\epsilon}\frac{p^2-1}{p^2+1}S_2, \tag{19}$$

$$\alpha_4 = \frac{kT}{2\epsilon}\left[\frac{p^2-1}{p^2+1}\right]^2 \frac{2}{35}\left(7-5S_2-2S_4\right), \tag{20}$$

$$\alpha_5 + \alpha_6 = \frac{kT}{\epsilon}\left[\frac{p^2-1}{p^2+1}\right]^2 \frac{1}{7}\left(3S_2+S_4\right). \tag{21}$$

B. Asymmetric stress tensor

Now we will try to follow the Kuzuu-Doi way of analyzing the asymmetric part of the stress tensor. The solution of Eq. (7) can be performed in the form of a perturbation series

$$f = f_0 + f_1 + \cdots , \tag{22}$$

where f_0 denotes the equilibrium distribution function and f_1 is the first-order perturbation in a small velocity gradient. Equation (7) can be rewritten by introducing the operator ζ

$$\zeta f = -\partial_k \left(\partial_k f + \frac{f_0}{kT} \partial_k U[f] + \frac{f}{kT} \partial_k U[f_0] \right). \tag{23}$$

The first two terms in (7) will read

$$0 = \epsilon \partial_k \left(\partial_k f_0 + \frac{f_0}{kT} \partial_k U[f_0] \right) \tag{24}$$

and

$$0 = -\epsilon \zeta f_1 - \partial_k (f_0 \Omega_k). \tag{25}$$

Let λ_n be an eigenvalue of ζ, and ϕ_n and ψ_n be the corresponding right-hand and left-hand eigenfunctions

$$\zeta \phi_n = \lambda_n \phi_n , \tag{26}$$

$$\zeta^\dagger \psi_n = \lambda_n \psi_n . \tag{27}$$

Since the eigenfunctions ψ_n and ϕ_n are orthogonal, the normalization condition reads

$$\langle \psi_m , \phi_n \rangle = \delta_{mn} . \tag{28}$$

The solution f_1 can be expressed in the form of an infinite series of $\{\phi_n\}$

$$f_1 = \sum_{n=1}^{\infty} a_n \phi_n . \tag{29}$$

Substituting (29) into (25), and using the orthonormal condition, one can obtain

$$\epsilon \lambda_n a_n = \langle \Omega_k \partial_k \psi_n \rangle . \tag{30}$$

This equation has a solution if $\lambda_n > 0$ for all n. However, the lowest eigenvalue λ_0 is zero. To see this let us consider an operation of rotating the director $\vec{n}$ by a small angle $\vec{\vartheta}$:

$$\vec{n} \to \vec{n}' = \vec{n} + \vec{\vartheta} \times \vec{n}, \tag{31}$$

which changes f_0 as

$$f_0 \to f_0' = f_0 + \vartheta_k \partial_k^{(n)} f_0 , \tag{32}$$

where $\partial_k^{(n)} = \epsilon_{ijk} n_i \frac{\partial}{\partial n_j}$ and $\partial_k^{(n)} f_0(\vec{n} \cdot \vec{a}) = -\partial_k f_0(\vec{n} \cdot \vec{a})$. Now both f_0 and f_0' must satisfy (24). This condition can be written as

$$\zeta[\vartheta_k \partial_k^{(n)} f_0] = 0. \tag{33}$$

This indicates that $\lambda_0 = 0$ and the right-hand eigenfunction ϕ_0 is

$$\phi_0 = \vartheta_k \partial_k^{(n)} f_0 = -\vartheta_k \partial_k f_0 . \tag{34}$$

Thus, from (30) we have

$$0 = \langle \Omega_k \partial_k \psi_0 \rangle . \tag{35}$$

This condition determines the director. It will be shown that Eq. (35) is equivalent to the second constitutive Leslie equation (6).

Substituting the explicit form of $\vec{\Omega}$ (8) into (35), after some calculation one obtains the condition

$$\left[\frac{p^2 - 1}{p^2 + 1} A_{\alpha\beta} + g^a_{\alpha\beta} \right] : \langle a_\alpha (\vec{a} \times \vec{\partial} \psi_0)_\beta \rangle = 0. \tag{36}$$

Now we have to establish ψ_0. From (23), the Hermitian conjugate operator of ζ can be obtained as (see Appendix A)

$$f_0 \zeta^\dagger \psi = [\partial_k [f_0(\vec{a}_1) \partial_k \psi(\vec{a}_1)] + f_0(\vec{a}_1) \beta \int K(\vec{a}_1, \vec{a}_2) \partial_k [f_0(\vec{a}_2) \partial_k \psi(\vec{a}_2)] d\vec{a}_2]. \tag{37}$$

Setting $\psi = \psi_0$ and noticing that $\zeta^\dagger \psi_0 = 0$, (37) can be written in the form

$$\phi(\vec{a}_1) = -f_0(\vec{a}_1) U[\phi(\vec{a}_1)], \tag{38}$$

where $\phi(\vec{a}_1)$ denotes

$$\phi(\vec{a}_1) = \partial_k [f_0(\vec{a}_1) \partial_k \psi_0(\vec{a}_1)]. \tag{39}$$

On the other hand, from (24) it emerges that

$$\partial_k f_0 = -\frac{f_0}{kT} \partial_k U[f_0]. \tag{40}$$

Multiplying (40) by ϑ_k and using (34) one arrives at the expression

$$\phi_0(\vec{a}_1) = -f_0(\vec{a}_1) U[\phi_0(\vec{a}_1)]. \tag{41}$$

It is the same form as (38), so $\phi_0 = \phi$ and we can replace the left-hand side of (39) by $-\vartheta_k \partial_k f_0$, which leads to the kinetic equation

$$\frac{\partial^2 \psi_0}{\partial \theta^2} + \left(\cot\theta - \frac{1}{kT} \frac{\partial U_0}{\partial \theta} \right) \frac{\partial \psi_0}{\partial \theta} + \frac{1}{\sin^2\theta} \frac{\partial^2 \psi_0}{\partial \phi^2} = -(\vartheta_k e_k) \frac{1}{kT} \frac{\partial U_0}{\partial \theta}, \tag{42}$$

where $\vec{e}$ is a unit vector parallel to $\partial \vec{u} / \partial \phi$ and $U_0 = U[f_0]$. Since $\vartheta_k e_k$ is a linear combination of $\cos\phi$ and $\sin\phi$, ψ_0 can be written as

$$\psi_0(\theta, \phi) = \vec{\vartheta} \cdot \vec{e} g(\cos\theta). \tag{43}$$

Substituting (43) into (42) one can get

$$\frac{\partial^2 g}{\partial \theta^2} + \left(\cot\theta - \frac{1}{kT} \frac{\partial U_0}{\partial \theta} \right) \frac{\partial g}{\partial \theta} - \frac{g}{\sin^2\theta} = -\frac{1}{kT} \frac{\partial U_0}{\partial \theta}. \tag{44}$$

The function ψ_0 can be obtained as it is shown in the Appendix in [8]. By the use of it Eq. (36) can be expressed as

$$\vec{n} \times \left[\frac{p^2-1}{p^2+1} S_2 \mathbf{A}\cdot\vec{n} - \frac{1}{2kT}\left\langle g\frac{\partial U_0}{\partial \theta}\right\rangle \mathbf{g}^a\cdot\vec{n}\right] = 0. \quad (45)$$

To obtain exactly Eq. (6) from Eq. (45) we have to multiply the latter by a certain constant. By virtue of the Parodi relation (4) and the form of $\alpha_2+\alpha_3$ from (19) it emerges that this constant should be $-kT/\epsilon$. Then the expressions for the rotational viscosity coefficients will be

$$\gamma_1 = \frac{1}{2\epsilon}\left\langle g\frac{\partial U_0}{\partial \theta}\right\rangle, \quad (46)$$

$$\gamma_2 = -\frac{kT}{\epsilon}\frac{p^2-1}{p^2+1}S_2 \ . \quad (47)$$

IV. THE OSIPOV-TERENTJEV APPROACH TO HYDRODYNAMICS

A. Molecular expressions for the Leslie coefficients

The idea of Osipov and Terentjev of how to obtain viscous coefficients is to average the expression for the microscopic stress tensor (13) with an appropriate nonequilibrium distribution function determined by the kinetic equation (7). In the equilibrium case the distribution function depends only on the angle θ between the director and the orientation of the molecule. As far as the flowing nematic liquid crystal in the molecular field approximation is concerned, the nonequilibrium single-particle distribution function must depend, due to the broken cylindrical symmetry, on two angles $f = f(\theta,\phi)$. In the case of small velocity gradients this function can be written in the form of $f = f_0(1+h)$, where f_0 is the local equilibrium distribution function and the small correction h is proportional to the velocity gradients.

The general expression for h has the form [9]

$$\begin{aligned} h = {} & \rho_0 n_\alpha n_\beta A_{\alpha\beta} + \rho_s n_\alpha e_\beta A_{\alpha\beta} + \rho_a n_\alpha e_\beta g^a_{\alpha\beta} \\ & + \rho_2 e_\alpha e_\beta A_{\alpha\beta}, \end{aligned} \quad (48)$$

where $\vec{n}$ is the director, $\vec{e}$ is the unit vector perpendicular to the director, $\mathbf{A}$ and $\mathbf{g}^a$ are symmetric and asymmetric parts of the velocity gradient, and ρ_i are correction functions dependent only on the angle θ. The relationships among the considered vectors and angles are

$$\vec{a} = \vec{n}\cos\theta + \vec{e}\sin\theta, \quad (49)$$

$$e_x = \cos\phi, \quad e_y = \sin\phi, \quad e_z = 0 \quad (50)$$

The macroscopic viscous stress tensor can be calculated due to the formula

$$\sigma_{\alpha\beta} = \int f\sigma^{micr}_{\alpha\beta} d\vec{a} = \int f_0 h \sigma^{micr}_{\alpha\beta} d\vec{a}. \quad (51)$$

Comparing the particular results obtained from the formula (51) to the form of the Leslie stress tensor, one can obtain the corresponding Leslie coefficients, provided functions ρ in the correction h are known.

For the rotational coefficients we have obtained the expressions (see Appendix B)

$$\gamma_1 = \int f_0 \frac{\partial U_0}{\partial\theta}\rho_a d(\cos\theta), \quad (52)$$

$$\gamma_2 = -\int f_0 \frac{\partial U_0}{\partial\theta}\rho_s d(\cos\theta). \quad (53)$$

The integral (52) was previously obtained by Kuzuu and Doi [8] and by Osipov and Terentjev [9].

For the coefficients due to the symmetric part of the stress tensor we have obtained the expressions

$$\begin{aligned} \alpha_1 = C\int f_0\Big\{ & 3kT\Big[\rho_0(3\cos^2\theta - 1) \\ & +\rho_2\left(\frac{3}{4}\sin^2\theta - \cos^2\theta\right) - \rho_s\sin(2\theta)\Big] \\ & +\frac{1}{2}\frac{\partial U_0}{\partial\theta}[(1.75\rho_2 - 3\rho_0)\sin(2\theta) \\ & -2\rho_s\cos(2\theta)]\Big\} d(\cos\theta), \end{aligned} \quad (54)$$

$$\begin{aligned} \alpha_2+\alpha_3 = -C\int f_0\Big(& 3kT\rho_a\sin 2\theta \\ & +\frac{\partial U_0}{\partial\theta}\rho_a\cos(2\theta)\Big) d(\cos\theta), \end{aligned} \quad (55)$$

$$\begin{aligned} \alpha_5+\alpha_6 = C\int f_0\Big[& 3kT\left(\rho_s\sin\theta\cos\theta - \frac{1}{2}\rho_2\sin^2\theta\right) \\ & +\frac{1}{2}\frac{\partial U_0}{\partial\theta}\left(\rho_s\cos(2\theta) - \frac{1}{2}\rho_2\sin(2\theta)\right)\Big] d(\cos\theta), \end{aligned} \quad (56)$$

$$\alpha_4 = C\int f_0\left(3kT\frac{1}{2}\rho_2\sin^2\theta + \frac{1}{4}\frac{\partial U_0}{\partial\theta}\rho_2\sin(2\theta)\right) d(\cos\theta), \quad (57)$$

where $C = \frac{p^2-1}{p^2+1}$. These expressions are different from those introduced in [10], where the authors did not take into account the term $3kT(a_\alpha a_\beta - \delta_{\alpha\beta}/3)$ as a part of the microscopic stress tensor in the derivation of microscopic formulas of the Leslie coefficients. All viscosity coefficients can be completely determined provided that we are able to determine the functions $\rho_a, \rho_{s,}\rho_0, \rho_2$.

B. Kinetic equation

The kinetic equation (7) can be expressed explicitly in terms of the coordinates θ and ϕ

$$\dot{f} - \epsilon^2 \left[\frac{\partial^2 f}{\partial\theta^2} + \left(\cot\theta + \frac{1}{kT}\frac{\partial U_0}{\partial\theta}\right)\frac{\partial f}{\partial\theta} + \frac{f}{kT}\left(\frac{\partial^2 U_0}{\partial\theta^2} + \cot\theta\frac{\partial U_0}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 f}{\partial\phi^2}\right]$$

$$= -\epsilon\left[\frac{\partial f}{\partial\theta}\left(\frac{p^2-1}{p^2+1}A_{bj}[n_b n_j \cos(2\theta) + (e_b e_j - n_b n_j)\sin\theta\cos\theta] - g_{bj} n_b e_j\right)\right.$$
$$\left. + f\frac{p^2-1}{p^2+1}A_{bj}[-3n_b e_j \sin(2\theta) + \tfrac{3}{2}\cos(2\theta)(e_j e_b - n_j n_b)(n\times e)_b(n\times e)_j - \tfrac{1}{2}e_b e_j - \tfrac{1}{2}n_b n_j]\right], \tag{58}$$

where terms proportional to the velocity gradients are placed on the right-hand side of the equation. The solutions of this equation should be linear in $\partial_\alpha v_\beta$, so on the right-hand side we can put f_0 instead of f. The left-hand side of (58) transforms into

$$\dot{f} - \epsilon^2 f_0\left[\frac{\partial^2 h}{\partial\theta^2} + \left(\cot\theta - \frac{1}{kT}\frac{\partial U_0}{\partial\theta}\right)\frac{\partial h}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2 h}{\partial\phi^2}\right]. \tag{59}$$

In the stationary case $\dot{f}$ is equal to zero, so in a further analysis we can omit this term.

Taking into account the dependence on ϕ of the function h, we can find the second derivative of h

$$\frac{\partial^2 h}{\partial\phi^2} = -\rho_s A_{\alpha\beta} n_\alpha e_\beta - \rho_a g^a_{\alpha\beta} n_\alpha e_\beta$$
$$+\rho_2[-2e_\alpha e_\beta + 2(n\times e)_\alpha (n\times e)_\beta], \tag{60}$$

where we have used the relations

$$\frac{\partial e_\beta}{\partial\phi} = (n\times e)_\beta, \tag{61}$$

$$\frac{\partial (n\times e)_\beta}{\partial\phi} = -e_\beta. \tag{62}$$

Using the equality

$$(n\times e)_\alpha (n\times e)_\beta = \delta_{\alpha\beta} - n_\alpha n_\beta - e_\alpha e_\beta \tag{63}$$

and noticing that in the case of incompressible systems the term $\delta_{\alpha\beta}A_{\alpha\beta}$ vanishes, we eventually come up with four differential equations for the functions ρ_s,ρ_a,ρ_2,ρ_0 by comparing similar terms on the left- and right-hand sides of (58):

$$\frac{\partial^2\rho_a}{\partial\theta^2} + \left(\cot\theta - \frac{1}{kT}\frac{\partial U_0}{\partial\theta}\right)\frac{\partial\rho_a}{\partial\theta} = \frac{\rho_a}{\sin^2\theta} + \frac{1}{\epsilon kT}\frac{\partial U_0}{\partial\theta}, \tag{64}$$

$$\frac{\partial^2\rho_s}{\partial\theta^2} + \left(\cot\theta - \frac{1}{kT}\frac{\partial U_0}{\partial\theta}\right)\frac{\partial\rho_s}{\partial\theta}$$
$$= \frac{\rho_s}{\sin^2\theta} + \frac{1}{\epsilon}\frac{p^2-1}{p^2+1}\left[-\frac{1}{kT}\frac{\partial U_0}{\partial\theta}\cos(2\theta) - 3\sin(2\theta)\right], \tag{65}$$

$$\frac{\partial^2\rho_2}{\partial\theta^2} + \left(\cot\theta - \frac{1}{kT}\frac{\partial U_0}{\partial\theta}\right)\frac{\partial\rho_2}{\partial\theta}$$
$$= \frac{4\rho_2}{\sin^2\theta} - \frac{1}{2\epsilon}\frac{p^2-1}{p^2+1}\left[\frac{1}{kT}\frac{\partial U_0}{\partial\theta}\sin(2\theta) - 3\cos(2\theta) + 3\right], \tag{66}$$

$$\frac{\partial^2\rho_0}{\partial\theta^2} + \left(\cot\theta - \frac{1}{kT}\frac{\partial U_0}{\partial\theta}\right)\frac{\partial\rho_0}{\partial\theta}$$
$$= \frac{2\rho_2}{\sin^2\theta} + \frac{1}{2\epsilon}\frac{p^2-1}{p^2+1}\left[\frac{1}{kT}\frac{\partial U_0}{\partial\theta}\sin(2\theta) - 3\cos(2\theta) - 3\right]. \tag{67}$$

In Refs. [9] and [10] Osipov and Terentjev have assumed that the time relaxation along the ϕ axis is much smaller than the time of reorientation with respect to the angle θ, so they neglected the term with ϕ. The simplest test to check whether this assumption is correct is, for instance, to compare the numerical solutions of Eqs. (64)–(67) with the solutions of the analogical equations deprived of the ϕ terms. It turns out that both these cases differ significantly. One can also find justification of this argument in [23] and [24]. Although the problem of the ϕ term in the kinetic equation has already been pointed out, there is no systematical analysis of its solutions. With the object of obtaining viscosity coefficients, we have provided such an analysis in the standard manner.

Equations (64)–(67) are linear, nonhomegenous differential equations of second order. A general solution of an equation of that type can be performed as a sum of a particular solution of nonhomogeneous differential equation, if we are able to find or guess it, and the general solution of a homogeneous differential equation

$$G_{\mathrm{NE}} = G_{\mathrm{HE}} + P_{\mathrm{NE}}, \tag{68}$$

where G_{HE} denotes the general solution of a homogeneous equation (GSHE), P_{NE} the particular solution of a nonhomogeneous equation (PSNE), and G_{NE} the general solution of a nonhomogenous equation (GSNE).

G_{HE} is dependent on two integral constants that are determined by the boundary and normalization conditions: (a) values of the functions ρ_s,ρ_a,ρ_2,ρ_0 should be symmetrical at the beginning and the end of the interval of integration (0 and π) which imposes that they should be constructed only from the even Legendre polynomials and (b) the integral $\int f_0 h d(\cos\theta) d\phi$ should vanish to fulfill the normalization condition.

We have noticed that the particular solution of (65) is

$$\rho_s = \frac{1}{2\epsilon}\frac{p^2-1}{p^2+1}\sin(2\theta). \tag{69}$$

It is apparent that conditions (a) and (b) are automatically fulfilled in this case. Fortunately we happen to find the desired solution for ρ_s. (While the GSHE is equal to 0, the GSNE is equal to the PSNE.)

For (66) and (67) the particular solutions are

$$\rho_2 = \frac{1}{2\epsilon}\frac{p^2-1}{p^2+1}\sin^2\theta, \tag{70}$$

$$\rho_0 = -\frac{1}{2\epsilon}\frac{p^2-1}{p^2+1}\sin^2\theta. \tag{71}$$

Neither fulfills the condition of normalization (b).

To find the desired solutions that would be in agreement with conditions (a) and (b) we return to the homogeneous equations for ρ_2 and ρ_0

$$\frac{\partial^2\rho_2}{\partial\theta^2} + \left(\cot\theta - \frac{1}{kT}\frac{\partial U_0}{\partial\theta}\right)\frac{\partial\rho_2}{\partial\theta} - \frac{4\rho_2}{\sin^2\theta} = 0, \tag{72}$$

$$\frac{\partial^2\rho_0}{\partial\theta^2} + \left(\cot\theta - \frac{1}{kT}\frac{\partial U_0}{\partial\theta}\right)\frac{\partial\rho_0}{\partial\theta} - \frac{2\rho_2}{\sin^2\theta} = 0. \tag{73}$$

The standard method of tackling this problem is to evaluate the functions ρ_2 and ρ_0 in a series of Legendre polynomials P_i $(i = 0, 1, \ldots)$

$$\rho_2 = \sum a_i P_i \ , \tag{74}$$

$$\rho_0 = \sum b_i P_i \ . \tag{75}$$

The boundary condition imposes that only even numbers of i should be taken into account. The normalization condition sets values of a_0 and b_0. Other coefficients a_i and b_i can be found by the use of an appropriate numerical procedure for solving a set of linear algebraic equations.

We can also try to solve Eqs. (64)–(67) in a purely numerical manner, treating them with a procedure for solving differential equations. This method was used to find out the solution of (64).

V. EQUIVALENCE OF OT AND KD APPROACHES

Now we would like to show that the OT and KD theories are equivalent. We will analyze the expressions for viscosity coefficients obtained in these two approaches. Let us look at the expression (11). We can notice that it is the same as the expression for the symmetric stress tensor with which we have started our considerations in the OT way. On the other hand, we can also notice that it is obtained from the right-hand side of (7), which formally can be treated as a homogeneous equation

$$\partial_k(\partial_k f - \Gamma_k/kTf) = 0. \tag{76}$$

So for each function performing (76), the right-hand side of (7) vanishes. Only functions that are not solutions of the homogeneous equation (76) make a contribution into viscosity coefficients and, despite the fact that they do not fulfill the normalization condition, can be regarded as candidates for averaging functions in (11). In the Osipov-Terentjev approach these functions are (69)–(71). The application of them to the expressions (54)–(57) leads after some calculations *exactly* to the expressions (18)–(21). This result can be treated as a convincing proof of the correctness of two different KD and OT approaches. Another important feature of the viscosity theory is the Parodi relation

$$\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5 \ , \tag{77}$$

which equals the symmetric $\alpha_2 + \alpha_3$ to the rotational γ_2.

In the OT approach we obtain that the following equality should hold:

$$-\frac{p^2-1}{p^2+1}\int f_0[6kT\sin\theta\cos\theta + \frac{\partial U_0}{\partial\theta}\cos(2\theta)]\rho_a d(\cos\theta)$$

$$= \int f_0 \frac{\partial U_0}{\partial\theta}\rho_s d(\cos\theta), \tag{78}$$

which can be rewritten as

$$\int f_0 \rho_a L \rho_s d(\cos\theta) = \int f_0 \rho_s L \rho_a d(\cos\theta), \tag{79}$$

where L is the operator

$$L = \frac{\partial^2}{\partial\theta^2} + \left(\cot\theta - \frac{1}{kT}\frac{\partial U_0}{\partial\theta}\right)\frac{\partial}{\partial\theta} - \frac{1}{\sin^2\theta}. \tag{80}$$

A proof of (79) can be found in Appendix C.

VI. VISCOUS PROPERTIES OF MBBA

To apply the above theories to any system one needs the equilibrium distribution function (EDF) $f_0 = \exp(-\beta U_0)$. In further analysis we used the EDF obtained in the standard second virial approximation of the density functional theory with the intermolecular potential of the Lennard-Jones type [25,26]

$$U = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^m - \left(\frac{\sigma}{r}\right)^n\right], \tag{81}$$

where m,n,ϵ are characteristic parameteres of the above potential, $\vec{r}$ is the vector that separates the centers of two molecules, and σ, due to Ruijgrok [25,26], is a function dependent on orientations of molecules $\vec{n}_1$,$\vec{n}_2$ and on the unit vector $\vec{\Delta}$ pointed in the direction of $\vec{r}$:

$$\sigma = \sigma_0 \left[1 + S_1(\vec{\Delta}\cdot\vec{n}_1)^2 + S_1(\vec{\Delta}\cdot\vec{n}_2)^2 - S_2(\vec{n}_1\cdot\vec{n}_2)^2\right] . \tag{82}$$

The parameters σ_0, S_1, S_2 are phenomenological parameters connected with shape and size of the molecule. In this approximation the necessary condition for the minimum of the free energy allows us to obtain the desired EDF, which has the form [25,26]

$$f_0(x) = \exp(c_0 + c_1 x^2 + c_2 x^4 + c_3 x^6), \tag{83}$$

where $x = \cos\theta$ and the coefficients c_i are the numbers established by the necessary condition equation.

Having obtained EDF it is possible to calculate a number of static properties such as the temperature of the phase transition, order parameters, energy, or elastic constants. Now the problem is how to fit potential parameters in order to obtain a satisfactory comparison to experimental data for a given compound. It turns out that it is sufficient to take only two different values of the K_1 elastic splay constant and the temperature of nematic-isotropic transition to obtain a good fitting of potential parameters that leads to satisfactory agreement of all possible static properties with experimental data.

Thus, for the mean potential U_0, necessary in hydrodynamics, we can use the expression

$$U_0 = -kT(c_0 + c_1 x^2 + c_2 x^4 + c_3 x^6). \tag{84}$$

Applying the mean potential (84) with coefficients c_i calculated for the case of MBBA [25] to the expressions (52)–(57), we obtain the viscosity coefficients characteristic for MBBA.

In Fig. 1 numerical results for the integral (52) due to γ_1 are introduced and its position is compared to the experimental data. The difference between one curve and the other corresponds to the diffusion coefficient $\epsilon_{\text{eff}} = \epsilon/kT$. By the use of numerical fitting we have found the curve for it, which we will use in our further numerical calculations.

Since, γ_2 is a simple linear function of S_2, we can check the accuracy of the result obtained for the diffusion ϵ/kT by comparing it to the similar value emerging from experimental data for γ_2 and S_2 [27]. This is shown in Fig. 2.

Taking into account the diffusion coefficient, finally we present the following curves for γ_1 (Fig. 3) and γ_2 (Fig. 4). Coefficients γ_1 and γ_2 are drawn in comparison with the experimental data from paper [27], which are recommended as model data. The agreement between theory and experiment is very good.

This is more apparent from the analysis of Fig. 5, where the temperature dependence of the extinction angle Θ is presented. Since $\cos\Theta$ is the ratio between γ_1 and γ_2, this result is obtained without taking into account any fitting for the diffusion coefficient. Such satisfactory agreement can be a convincing proof of the accuracy of the theory. The dashed line presents results of the Osipov-Terentjev theory from the Ref. [28]. The intermolecular potential used therein leads to the maximum agreement with experimental values of the extinction angle about 15%. Moreover, it is not checked whether this potential really describes a mesophase state and gives a nematic solution. In our case we are completely sure that our potential describes a nematic. Moreover, it is possible to predict all static properties for it, as it has been introduced in [25].

The ratio p=length/width found in [28] is about 2, while it is expected to be 5. In [28] the authors explain that two MBBA molecules form a rotating cluster or a dimer; however, there is no experimental evidence about it. In our considerations this ratio is equal to 5 and it is found to be the same at each temperature, contrary to the results in [28].

In Fig. 6 we show numerical results for the integrals from (79): circles represent the right-hand side and the solid curve represents the left-hand side integral. Since the Parodi relation is fulfilled exactly, the fact that both

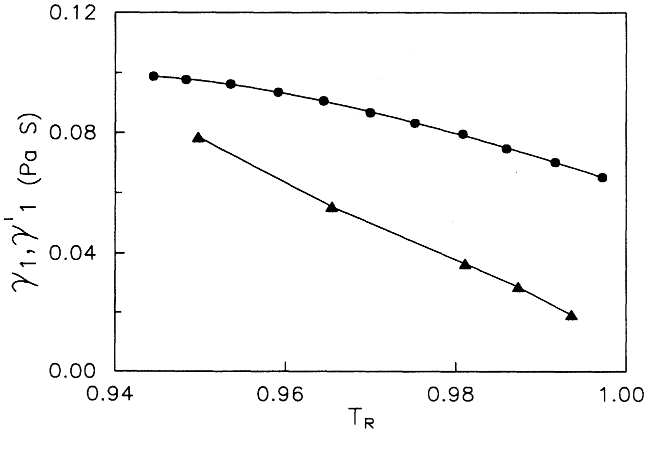

FIG. 1. Rotational viscosity coefficient for MBBA γ_1. Circles represent results from our theory (without the diffusion coefficient) and triangles from [27].

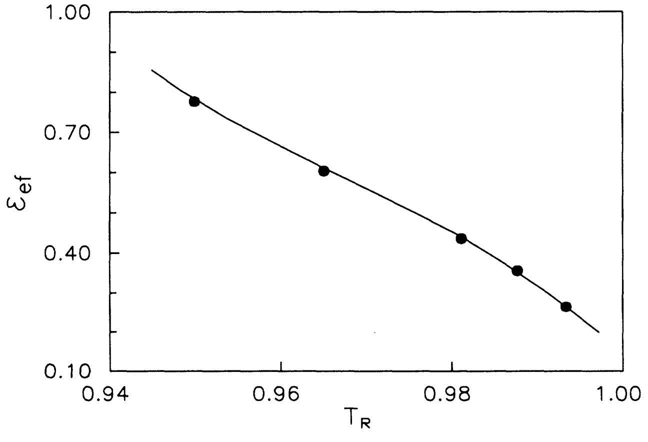

FIG. 2. Effective diffusion coefficient ϵ_{eff} obtained by the use of fitting our results for γ_1 to the experimental data. Circles are obtained on the basis of data for S_2 and γ_2 from [27].

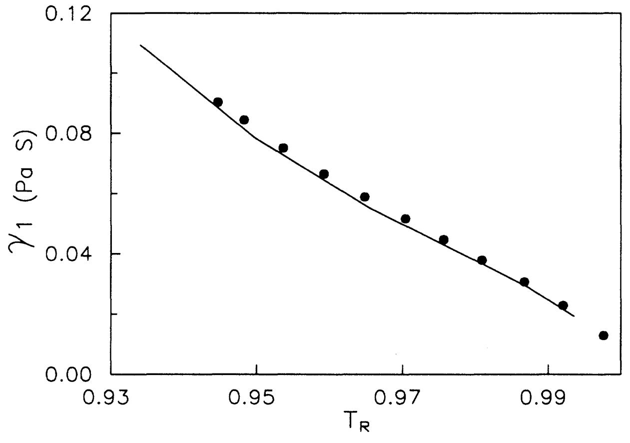

FIG. 3. Rotational viscosity coefficient γ_1 for MBBA. Circles represent results from our theory, including fitting for the diffusion coefficient, and triangles from [27].

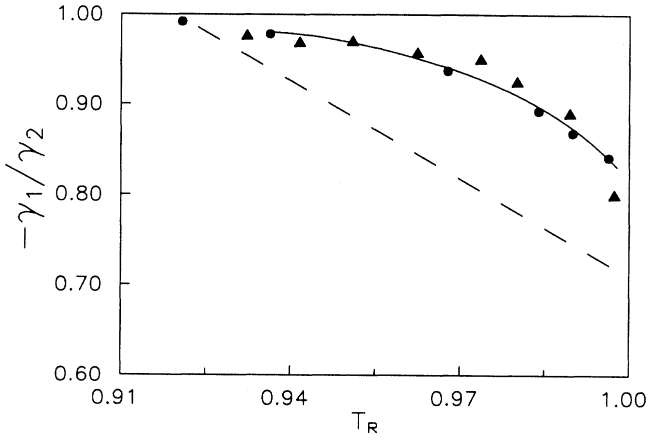

FIG. 5. Extinction angle Θ for MBBA ($\cos\Theta = -\gamma_1/\gamma_2$). The solid line represents results from our theory. The dashed line from OT theory [28], circles from [27], and triangles from [29].

these curves are not identical is due to the accuracy of the procedure for solving differential equations.

In Figs. 7 and 8 we show numerical results for α_1 and $\alpha_5+\alpha_6$, respectively. The disagreement between theoretical and experimental results is probably mainly caused by the experimental errors. It is worth remarking here that the Leslie coefficients should drop to zero while approaching the critical temperature (the reduced temperature is equal to 1), while it is apparent from Figs. 7 and 8 that experimental data tend to vanish before reaching $T = 1$.

In Fig. 9 we introduce values of α_4 and its comparison to the experimental data. Values obtained from the theory are much lower than values measured in experiment. To explain we have to pay attention to the fact that the α_4 considered in our theory is the nematic contribution to α_4, which should vanish since the nonequilibrium contributions to the distribution function disappear. The theories of Osipov-Terentjev and Kuzuu-Doi do not describe viscosity properties of the isotropic nematic system and the determination of isotropic part of α_4 is beyond the scope of these theories. On the other hand, from the analysis of the experimental data it emerges that this value must consist of these two parts since it drops to a finite value at $T = 1$. What is also apparent from Fig. 9 is that the isotropic influence on α_4 is much stronger than the nematic effect. From all these results it can be concluded that the Osipov-Terentjev statistical approach or the equivalent Kuzuu-Doi theory with the application of the Ruijgrok potential provides a very satisfactory description of nematic viscosity and can be regarded as a complete theory at the molecular statistical level.

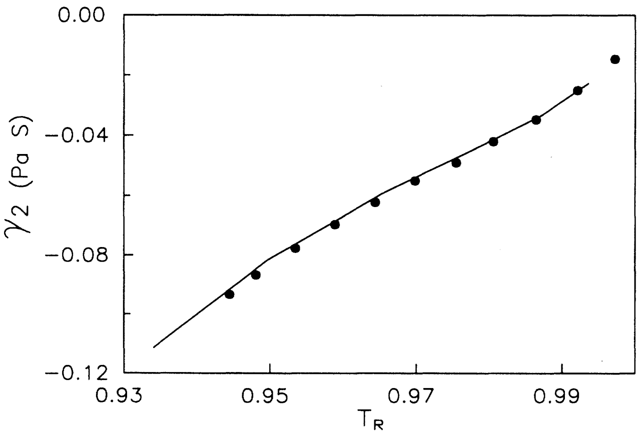

FIG. 4. Rotational viscosity coefficient γ_2 for MBBA. Circles represent results from our theory, including fitting for the diffusion coefficient, and triangles from [27].

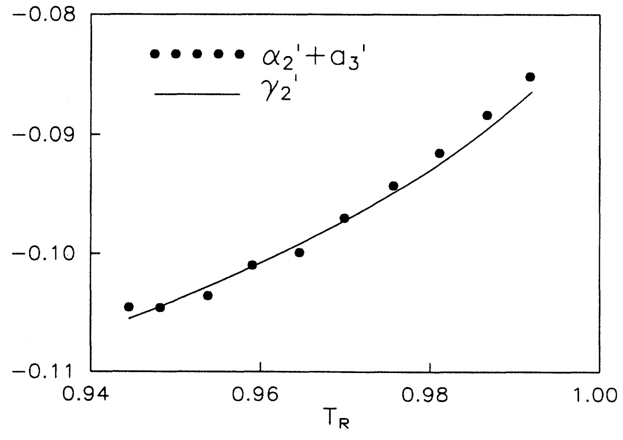

FIG. 6. Numerical results for the Parodi equality (79).

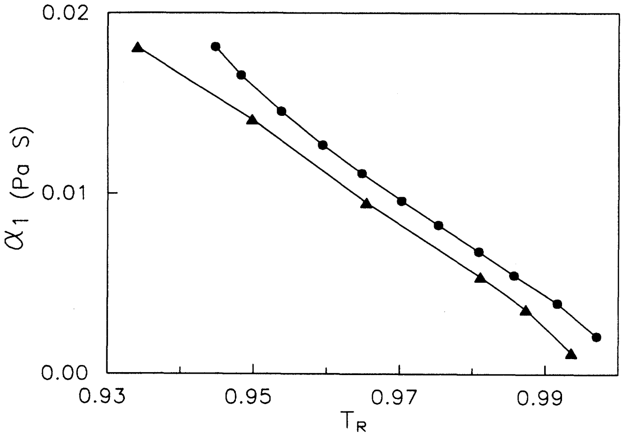

FIG. 7. Coefficient α_1 for MBBA. Circles represent results from our theory and triangles from [27].

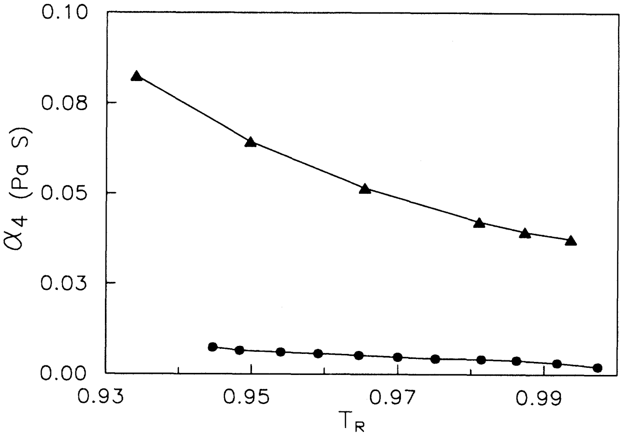

FIG. 9. Coefficient α_4 for MBBA. Circles represent results from our theory and triangles from [27].

VII. CONCLUSION

The idea of Osipov and Terentjev has been used to obtain the improved general microscopic expressions for the Leslie coefficients. The difference between our expressions and those presented in [10] is mainly caused by omitting the term $3kT(a_\alpha a_\beta - \delta_{\alpha\beta}/3)$ in the microscopic stress tensor in this paper. Only by the use of the exact expression for the microscopic stress tensor are we able to arrive at correct results.

We have paid attention to the fact that the symmetric part of the microscopic stress tensor must be enriched with the form factor $\frac{p^2-1}{p^2+1}$, contrary to the one used in theories so far. Only by including this form factor is it possible to fulfill the Parodi relation. In general, the Onsager relations, whose particular example is the Parodi relation, can be treated as a check of correctness of any transport theory.

In the case of platelike molecules this form factor is of special interest. Since in this case it has negative values, the lack of it can cause a change in sign of certain viscosity coefficients.

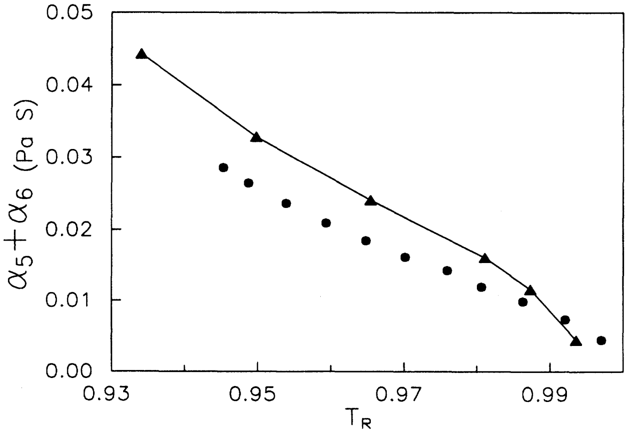

FIG. 8. Coefficient $\alpha_5 + \alpha_6$ for MBBA. Circles represent results from our theory and triangles from [27].

A systematic analysis of solutions of the kinetic equations has allowed us to show that the expressions for the Leslie coefficients in the OT approach can be transformed to a form that is exactly the same as that obtained by Kuzuu and Doi. It is the most important outcome of these considerations that both the KD and OT theories may lead to the same microscopic expressions for viscosity coefficients.

Information on the type of system appears in hydrodynamic theories mainly as the mean potential. This potential reflects the influence of the rest of the system on a given particle. It can be obtained from the equilibrium distribution function. In our consideration we have used the mean potential coming from the density functional theory on the basis of the Ruijgrok potential. The analytical form of this mean potential is a sixth-order polynomial of cosθ with coefficients c_i, which can be explicitly calculated from the necessary condition equation for the minimum of the free energy.

Using the mean potential adjusted to the case of MBBA we have found rotational and symmetric viscosity coefficients. The results have turned out to be in very good agreement with the experimental data.

The deviation of α_4 from the experimental data is suggested to be caused by the influence of the isotropic contribution on the experimental value, which cannot be established within the framework of the above theories. The Parodi relation is fulfilled exactly. This has been presented both analytically and numerically. From the figure showing the Parodi relation we can conclude about the influence of the mean potential and numerical errors especially for integrals that include the asymmetric function ρ_a. We can say that coefficients $\alpha_2+\alpha_3$ and γ_1 (both of them are dependent on ρ_a) are the most sensitive to the mean potential. The diffusion coefficient obtained from the fitting γ_2 to the experimental data has been compared to and found in very good agreement with the values obtained on the basis of the experimental data for

S_2 and γ_2.

The parameter p=(length)/(width) is found to be 5, which in the case of MBBA is correct, whereas from results of other works it is predicted to be about 2. The value 2 of the parameter p has been the reason for the suggestion that molecules of MBBA tend to form a cluster or dimer. However, there is no experimental evidence about this. Due to the results presented in this paper, we would rather say that the idea of dimers does not relate to MBBA.

There is a consistent connection between statics and hydrodynamics through the point of the mean potential and, as a matter of fact, the same intermolecular parameters determine static and hydrodynamic properties as well. To sum up, we can say that the hydrodynamic theories mentioned provide a complete description of viscosity properties at the molecular level.

APPENDIX A

The aim of this appendix is to find the Hermitian conjugate operator of ζ

$$\zeta\phi = -\partial_k\left(\partial_k\phi + \frac{f_0}{kT}\partial_k U[\phi] + \frac{\phi}{kT}\partial_k U[f_0]\right). \quad \text{(A1)}$$

Taking into account that by the use of operator $\vec{\partial}$ we can perform integration by parts (see [22]), let us analyze the expression

$$\begin{aligned}\int \psi\zeta\phi d\vec{a} &= \int \left(\partial_k\phi + \frac{f_0}{kT}\partial_k U[\phi] + \frac{\phi}{kT}\partial_k U[f_0]\right)\partial_k\psi d\vec{a}\\ &= \int \frac{\phi}{kT}\partial_k U_0 \partial_k\psi d\vec{a} - \int \phi\partial_k\partial_k\psi d\vec{a} - \int \frac{f_0}{kT}\partial_k\psi\partial_k \int K(\vec{a}_1,\vec{a}_2)\phi(\vec{a}_2)d\vec{a}_1 d\vec{a}_2\\ &= \int \left(-\phi\partial_k\partial_k\psi + \frac{\phi}{kT}\partial_k U_0\partial_k\psi\right)d\vec{a} + \frac{1}{kT}\int K(\vec{a}_1,\vec{a}_2)\phi(\vec{a}_2)\int \partial_k(f_0\partial_k\psi)d\vec{a}_1 d\vec{a}_2, \end{aligned} \quad \text{(A2)}$$

where $U_0 = U[f_0]$. The first term by virtue of (24) is equal to $-\partial_k(\phi\partial_k\psi)$, so setting $\phi = f_0$ we finally obtain

$$\begin{aligned} f_0\zeta^\dagger\psi = &-\partial_k[f_0(\vec{a}_1)\partial_k\psi(\vec{a}_1)]\\ &+\frac{f_0(\vec{a}_1)}{kT}\int K(\vec{a}_1,\vec{a}_2)\partial_k[f_0(\vec{a}_2)\partial_k\psi(\vec{a}_2)]d\vec{a}_2, \end{aligned} \quad \text{(A3)}$$

where we have used the state equation

$$\ln[f(\vec{a}_1)] = \frac{1}{kT}\int K(\vec{a}_1,\vec{a}_2)f(\vec{a}_2)d\vec{a}_2\ , \quad \text{(A4)}$$

where $f = e^{-\frac{U}{kT}}$.

APPENDIX B

Let us take into account the asymmetric part of the stress tensor. From Leslie's theory it has the form

$$\begin{aligned}\sigma_{\alpha\beta}^{\text{asym}} = &-\frac{1}{2}\gamma_2(n_\alpha n_\mu A_{\mu\beta} - n_\beta n_\mu A_{\mu\alpha})\\ &-\frac{1}{2}\gamma_1(n_\alpha N_\beta - n_\beta N_\alpha). \end{aligned} \quad \text{(B1)}$$

The equivalent microscopic expression reads

$$\sigma_{\alpha\beta}^{\text{asym}} = \int f_0(1+h)\sigma_{\alpha\beta}^{\text{asym,mic}}d\vec{a}\ , \quad \text{(B2)}$$

where

$$\sigma_{\alpha\beta}^{\text{asym,mic}} = \frac{1}{2}\left[a_\alpha\frac{\partial U}{\partial a_\beta} - a_\beta\frac{\partial U}{\partial a_\alpha}\right]. \quad \text{(B3)}$$

Since $U = U(\theta)$,

$$\vec{a} = \vec{n}\cos\theta + \vec{e}\sin\theta\ , \quad \text{(B4)}$$

and

$$\frac{\partial}{\partial\vec{a}} = (\vec{e}\cos\theta - \vec{n}\sin\theta)\frac{\partial}{\partial\theta} + \frac{\vec{n}\times\vec{e}}{\sin\theta}\frac{\partial}{\partial\phi}, \quad \text{(B5)}$$

then

$$\begin{aligned} a_\alpha\frac{\partial U}{\partial a_\beta} = &[n_\alpha e_\beta\cos^2\theta + (e_\alpha e_\beta - n_\alpha n_\beta)\sin\theta\cos\theta\\ &- - e_\alpha n_\beta\sin^2\theta]\frac{\partial U}{\partial\theta}. \end{aligned} \quad \text{(B6)}$$

Thus

$$\begin{aligned}\sigma_{\alpha\beta}^{\text{asym}} = &\int f_0(1+h)\frac{\partial U}{\partial\theta}[n_\alpha e_\beta\cos^2\theta + (e_\alpha e_\beta - n_\alpha n_\beta)\sin\theta\cos\theta - e_\alpha n_\beta\sin^2\theta - n_\alpha e_\beta\sin^2\theta\\ &-(e_\alpha e_\beta - n_\alpha n_\beta)\sin\theta\cos\theta + e_\alpha n_\beta\cos^2\theta]d\vec{a} = \int f_0(1+h)\frac{\partial U}{\partial\theta}\left[n_\alpha e_\beta - e_\alpha n_\beta\right]d\phi d(\cos\theta). \end{aligned} \quad \text{(B7)}$$

It is apparent that the equilibrium contribution to the asymmetric stress tensor vanishes due to the integration over the angle ϕ because integrals of odd number of e_α are equal to zero

$$\int_0^{2\pi} e_\alpha d\phi = 0, \quad \int_0^{2\pi} e_\alpha e_\beta e_\gamma d\phi = 0. \tag{B8}$$

Thus

$$\begin{aligned}\sigma_{\alpha\beta}^{\text{asym}} = & \int f_0 \frac{\partial U}{\partial\theta}[n_\alpha e_\beta - e_\alpha n_\beta] \\ & \times[\rho_0 n_\alpha n_\beta A_{\alpha\beta} + \rho_s n_\alpha e_\beta A_{\alpha\beta} \\ & + \rho_a n_\alpha e_\beta g^a_{\alpha\beta} + \rho_2 e_\alpha e_\beta A_{\alpha\beta}] d\phi d(\cos\theta).\end{aligned} \tag{B9}$$

We finally came up with the expression

$$\begin{aligned}\sigma_{\alpha\beta}^{\text{asym}} = & \int f_0 \frac{\partial U}{\partial\theta}[\rho_s(n_\alpha n_\mu A_{\mu\beta} - A_{\alpha\mu} n_\mu n_\beta) \\ & + \rho_a(n_\alpha n_\mu g^a_{\mu\beta} - g^a_{\mu\alpha} n_\beta n_\mu)] d(\cos\theta).\end{aligned} \tag{B10}$$

Comparing (B10) with (A1), we can get microscopic expressions for the rotational viscosity coefficients

$$\gamma_1 = \int f_0 \frac{\partial U}{\partial\theta} \rho_a d(\cos\theta), \tag{B11}$$

$$\gamma_2 = -\int f_0 \frac{\partial U}{\partial\theta} \rho_s d(\cos\theta). \tag{B12}$$

Using the same technique as above we can evaluate the symmetric part of the stress tensor.

APPENDIX C

In the derivation of the Parodi relation, the first and second derivatives of f_0 are

$$\frac{\partial f_0}{\partial\theta} = -\beta f_0 \frac{\partial U}{\partial\theta}, \quad \frac{\partial^2 f_0}{\partial\theta^2} = -\beta f_0 \frac{\partial^2 U}{\partial\theta^2} + \beta^2 f_0 \frac{\partial U}{\partial\theta}\frac{\partial U}{\partial\theta}\ . \tag{C1}$$

Using integration by parts we have

$$\begin{aligned}\int f_0\rho_a L\rho_s d(\cos\theta) = & \int f_0\rho_a\left[\frac{\partial^2}{\partial\theta^2} + \left(\cot\theta - \beta\frac{\partial U}{\partial\theta}\right)\frac{\partial}{\partial\theta} - \frac{1}{\sin^2\theta}\right]\rho_s d(\cos\theta) \\ & - \int \rho_s\left\{\frac{\partial^2}{\partial\theta^2}[f_0\sin\theta\rho_a] - \frac{\partial}{\partial\theta}\left[f_0\sin\theta\rho_a\left(\cot\theta - \beta\frac{\partial U}{\partial\theta}\right)\right] - f_0\sin\theta\rho_a\frac{1}{\sin^2\theta}\right\}d\theta \\ = & \int \rho_s\sin\theta\left[f_0\rho_a - \rho_a\frac{\partial^2 f_0}{\partial\theta^2} - 2\frac{\partial f_0}{\partial\theta}\left(\cot\theta\rho_a + \frac{\partial\rho_a}{\partial\theta}\right) - f_0\left(2\cot\theta\frac{\partial\rho_a}{\partial\theta} + \frac{\partial^2\rho_a}{\partial\theta^2}\right)\right]d\theta \\ & + \int \rho_s\sin\theta\left[\left(\frac{\partial f_0}{\partial\theta}\rho_a + \cot\theta f_0\rho_a + f_0\frac{\partial\rho_a}{\partial\theta}\right)\left(\cot\theta - \beta\frac{\partial U}{\partial\theta}\right)\right]d\theta \\ & - \int \rho_s\sin\theta f_0\rho_a\left(\frac{1}{\sin^2\theta} + \beta\frac{\partial^2 U}{\partial\theta^2}\right)d\theta - \int f_0\sin\theta\rho_s\rho_a\frac{1}{\sin^2\theta}d\theta\ .\end{aligned} \tag{C2}$$

By virtue of (C1) the expression (C2) can be rewritten

$$\begin{aligned} & -\int \beta f_0\rho_s\rho_a\sin\theta\left[\beta\frac{\partial U}{\partial\theta}\frac{\partial U}{\partial\theta} - \frac{\partial^2 U}{\partial\theta^2} - 2\cot\theta\frac{\partial U}{\partial\theta} + \frac{\partial U}{\partial\theta}\left(\cot\theta - \beta\frac{\partial U}{\partial\theta}\right)\right]d\theta \\ & - \int f_0\rho_a\rho_s\sin\theta\left(-1 - \cot^2\theta + \cot\theta\beta\frac{\partial U}{\partial\theta} + \frac{1}{\sin^2\theta} + \beta\frac{\partial^2 U}{\partial\theta^2} - \frac{1}{\sin^2\theta}\right)d\theta \\ & - \int f_0\rho_s\sin\theta\left\{\frac{\partial^2\rho_a}{\partial\theta^2} + \frac{\partial\rho_a}{\partial\theta}\left[-2\beta\frac{\partial U}{\partial\theta} + 2\cot\theta - \left(\cot\theta - \beta\frac{\partial U}{\partial\theta}\right)\right]\right\}d\theta \\ & = \int f_0\sin\theta\rho_s\left[\frac{\partial^2}{\partial\theta^2} + \left(\cot\theta - \beta\frac{\partial U}{\partial\theta}\right)\frac{\partial}{\partial\theta} - \frac{1}{\sin^2\theta}\right]\rho_a d\theta\ .\end{aligned} \tag{C3}$$

The last line in (C3) is equal to

$$\int f_0\rho_a L\rho_s d(\cos\theta)\ , \tag{C4}$$

which is the right-hand side of the Parodi relation.

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