The Viscosity Coefficients of Oriented Nematic and Nematic Discotic Liquid Crystals; Affine Transformation Model

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General expressions are derived for the anisotropy of the viscosity and for the Leslie coefficients governing the flow alignment subject to the assumption that the equipotential surfaces for the interaction of oriented nonspherical molecules in the nematic or nematic discotic phase of a liquid crystal are related to a spherical interaction potential by an affine transformation. In particular, for uniaxial particles, the seven independent viscosity coefficients of a nematic are given in terms of the two viscosity coefficients of a reference fluid of spherical particles and the axes ratio of the nonspherical molecules. The theory is compared with results from nonequilibrium molecular dynamics computer simulations and with experimental data.

Oriented nematic liquid crystals show a strong anisotropy of the viscosity [1–5]. Theoretical explanations of this behavior typical for anisotropic fluids fall into three categories. Firstly, phenomenological considerations which yield the number of independent viscosity coefficients and (Onsager) relations between them [6–9]; secondly, semi-microscopic (mesoscopic) theories which aim at giving the dependence of the viscosity coefficients on the order parameter [10–13]; and thirdly, microscopic (kinetic) theories. In the latter case, special model assumptions have to be introduced to obtain specific results.

In this article a fluid of perfectly ordered particles is considered; the equipotential surfaces are assumed to be ellipsoids (of revolution). This model has previously been used by Helfrich [14]. Here, some general results are presented which follow from an affine transformation linking both the interaction potential and the pair-correlation function of a fluid of nonspherical particles with those of spherical particles. Some consequences of the theory have already been tested in nonequilibrium molecular dynamics simulations and were compared with experiments [15]. Before the main points of this article are treated, the phenomenological description of the anisotropic viscosity is presented in order to introduce the various viscosity coefficients (Section 1). The affine transformation model for perfectly oriented molecules is introduced and its consequences are exploited (both for prolate and oblate particles) in Section 2. In particular, the seven independent viscosity coefficients of a nematic are related to the shear viscosity and the bulk viscosity of a reference fluid composed of spherical particles. These relations involve the axes ratio Q of the nonspherical particles which are modelled as ellipsoids of revolution. In Sect. 3 a comparison with results inferred from nonequilibrium molecular dynamics simulations and with experimental data is made.

1. Viscosity Coefficients

1.1. Phenomenological Ansatz for the Friction Pressure Tensor

The local momentum balance equation reads

$$\frac{\partial}{\partial t}(\varrho\, v_\mu) + \nabla_\nu(\varrho\, v_\nu\, v_\mu) + \nabla_\nu\, P_{\nu\mu} = 0, \tag{1}$$

where ϱ is the mass density. Cartesian components of the average flow velocity and the pressure tensor are denoted by v_μ and $P_{\nu\mu}$. The summation convention is used for Greek subscripts. The friction pressure tensor $p_{\nu\mu}$ is the difference between $P_{\nu\mu}$ and its equilibrium value $P^{\mathrm{eq}}_{\nu\mu}$:

$$P_{\nu\mu} = P^{\mathrm{eq}}_{\nu\mu} + p_{\nu\mu}. \tag{2}$$

With the help of the substantial derivative

$$\frac{d}{dt} = \frac{\partial}{\partial t} + v_\lambda\, \nabla_\lambda \tag{3}$$

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and with the continuity equation, (1) can be rewritten as

$$\varrho \frac{d}{dt} v_\nu + \nabla_\nu P^{\mathrm{eq}}_{\nu\mu} + \nabla_\nu p_{\nu\mu} = 0. \tag{4}$$

The viscosity coefficients occur in the (linear) relation which links the friction pressure $p_{\nu\mu}$ with the gradient of the velocity $\nabla_\nu v_\mu$. Like any second rank tensor, these quantities can be decomposed into their isotropic, antisymmetric and symmetric traceless parts; e.g.

$$\nabla_\nu v_\mu = \tfrac{1}{3} \nabla_\lambda v_\lambda \delta_{\mu\nu} + \varepsilon_{\nu\mu\lambda} \omega_\lambda + \gamma_{\nu\mu} \tag{5}$$

with the vorticity

$$\omega_\lambda = \tfrac{1}{2} \varepsilon_{\lambda\alpha\beta} \nabla_\alpha v_\beta \tag{6}$$

and the deformation rate tensor

$$\gamma_{\nu\mu} = \overline{\nabla_\nu v_\mu} = \tfrac{1}{2}(\nabla_\nu v_\mu + \nabla_\mu v_\nu) - \tfrac{1}{3} \nabla_\lambda v_\lambda \delta_{\mu\nu}. \tag{7}$$

The symbol $\overline{\ldots}$ refers to the symmetric traceless part of a tensor; $\varepsilon_{\mu\nu\lambda}$ is the (totally antisymmetric) isotropic tensor of rank three. For an anisotropic fluid characterized by the director field $\boldsymbol{n} = \boldsymbol{n}(t, \boldsymbol{r})$ and its corotational time derivative

$$N_\mu = \frac{d}{dt} n_\mu - \varepsilon_{\mu\nu\lambda} \omega_\nu n_\lambda, \tag{8}$$

the ansatz [5]

$$\begin{aligned} -p_{\nu\mu} = {} & \alpha_1 n_\nu n_\mu n_\lambda n_\varkappa \gamma_{\lambda\varkappa} + \alpha_2 n_\nu N_\mu + \alpha_3 N_\nu n_\mu \\ & + \alpha_4 \gamma_{\nu\mu} + \alpha_5 n_\nu n_\lambda \gamma_{\lambda\mu} + \alpha_6 \gamma_{\nu\lambda} n_\lambda n_\mu \\ & + \zeta_1 n_\lambda n_\varkappa \gamma_{\lambda\varkappa} \delta_{\mu\nu} + \zeta_2 n_\nu n_\mu \nabla_\lambda v_\lambda + \zeta_3 \nabla_\lambda v_\lambda \delta_{\mu\nu} \end{aligned} \tag{9}$$

is made, where the Leslie coefficients $\alpha_1, \ldots, \alpha_6$ and the coefficients $\zeta_{1,2,3}$ have the dimension of a viscosity. The standard expression for the friction pressure tensor of a nematic corresponds to (9) without the terms involving the ζ_i, $i = 1, 2, 3$. Decomposition of the pressure tensor corresponding to (5) leads to [8, 9, 16]

$$\begin{aligned} \overline{p_{\nu\mu}} = {} & -2\eta \gamma_{\nu\mu} - 2\tilde{\eta}_1 \overline{n_\nu n_\lambda \gamma_{\lambda\mu}} \\ & - 2\tilde{\eta}_2 \overline{n_\nu N_\mu} - 2\tilde{\eta}_3 \overline{n_\nu n_\mu} n_\lambda n_\varkappa \gamma_{\lambda\varkappa} \\ & - \zeta_2 \overline{n_\nu n_\mu} \nabla_\lambda v_\lambda, \end{aligned} \tag{10}$$

$$p^{\mathrm{a}}_{\nu\mu} = \gamma_1 (n_\nu N_\mu)^{\mathrm{a}} + \gamma_2 (n_\nu n_\lambda \gamma_{\lambda\mu})^{\mathrm{a}}, \tag{11}$$

$$\tfrac{1}{3} p_{\lambda\lambda} = -\eta_{\mathrm{V}} \nabla_\lambda v_\lambda - \varkappa n_\lambda n_\varkappa \gamma_{\lambda\varkappa}, \tag{12}$$

where the antisymmetric part $T^{\mathrm{a}}_{\nu\mu}$ of any 2nd rank tensor $T_{\nu\mu}$ is given by

$$T^{\mathrm{a}}_{\nu\mu} = \tfrac{1}{2}(T_{\nu\mu} - T_{\mu\nu}). \tag{13}$$

The viscosity coefficients occurring in (10–12) are related to those of (9) by

$$\eta = \tfrac{1}{2}[\alpha_4 + \tfrac{1}{3}(\alpha_5 + \alpha_6)], \tag{13a}$$

$$\begin{aligned} \tilde{\eta}_1 &= \tfrac{1}{2}(\alpha_5 + \alpha_6), \\ \tilde{\eta}_2 &= \tfrac{1}{2}(\alpha_2 + \alpha_3), \\ \tilde{\eta}_3 &= \tfrac{1}{2}\alpha_1, \end{aligned} \tag{14}$$

$$\begin{aligned} \gamma_1 &= \alpha_3 - \alpha_2, \\ \gamma_2 &= \alpha_6 - \alpha_5, \end{aligned} \tag{15}$$

$$\begin{aligned} \eta_{\mathrm{V}} &= \tfrac{1}{3}\zeta_2 + \zeta_3, \\ \varkappa &= \zeta_1 + \tfrac{1}{3}(\alpha_1 + \alpha_5 + \alpha_6). \end{aligned} \tag{16}$$

Two Onsager symmetry relations exist between the 9 viscosity coefficients considered so far:

$$2\tilde{\eta}_2 = \gamma_2 \tag{17}$$

or, equivalently,

$$\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5, \tag{17a}$$

and [9, 16]

$$\zeta_2 = \varkappa. \tag{18}$$

Relation (17a) is referred to as the Parodi equation [7]. For an isotropic fluid, all viscosity coefficients vanish except for the shear viscosity $\eta = \frac{1}{2}\alpha_4$ and the bulk viscosity $\eta_{\mathrm{V}} = \zeta_3$.

1.2. Miesowicz Viscosities

In a shear flow experiment, linear combinations of the viscosity coefficients introduced so far are measured. For the case of a plane Couette flow with the velocity in the x-direction and its gradient in the y-direction one has

$$\nabla \boldsymbol{v} = \gamma \boldsymbol{e}^y \boldsymbol{e}^x, \quad \boldsymbol{\omega} = -\tfrac{1}{2} \gamma \boldsymbol{e}^z,$$

with the constant shear rate

$$\gamma = \partial v_x / \partial y; \tag{19}$$

$\boldsymbol{e}^{x,y,z}$ are unit vectors parallel to the x-, y- and z-coordinate axes.

The Miesowicz viscosities [1–5, 17] η_i, $i = 1, 2, 3$, are defined by

$$p_{yx} = -\eta_i \gamma \tag{20}$$

with the director $\boldsymbol{n}$ parallel to the x, y, z-axes, respectively. Experimentally this case is realized when the orienting external (magnetic) field is strong enough to overcome the flow induced orientation [1–5]. The directly measurable Miesowicz coefficients are linked with the coefficients of (9–11) by

$$\begin{aligned}\eta_1 &= \tfrac{1}{2}(\alpha_4+\alpha_6+\alpha_3) = \eta + \tfrac{1}{6}\tilde{\eta}_1 + \tilde{\eta}_2 + \tfrac{1}{4}\gamma_1,\\ \eta_2 &= \tfrac{1}{2}(\alpha_4+\alpha_5-\alpha_2) = \eta + \tfrac{1}{6}\tilde{\eta}_1 - \tilde{\eta}_2 + \tfrac{1}{4}\gamma_1,\\ \eta_3 &= \tfrac{1}{2}\alpha_4 \qquad\qquad\quad\; = \eta - \tfrac{1}{3}\tilde{\eta}_1.\end{aligned} \tag{21}$$

A fourth coefficient is needed to characterize the shear viscosity. Following Helfrich [17], the quantity

$$\eta_{12} = 4\eta_{45} - 2(\eta_1+\eta_2) \tag{22}$$

is used where η_{45} is the viscosity for $\boldsymbol{n}$ parallel to $\boldsymbol{e}^x + \boldsymbol{e}^y$, i.e. under 45° with respect to the flow direction. Similar to (21), one has

$$\eta_{12} = \alpha_1 = 2\tilde{\eta}_3. \tag{23}$$

Notice that the antisymmetric part of the pressure tensor only contributes to η_1 and η_2 but not to η_3 and η_{12}.

1.3. Normal Pressure Effects

From the ansatz (9) or from (10) and (12) one infers the normal pressure differences

$$\begin{aligned}p_{xx} - p_{yy} &= \gamma\, n_x n_y\,[\gamma_2 + \eta_{12}(n_y^2 - n_x^2)], \qquad (24)\\ p_{zz} - \tfrac{1}{2}(p_{xx}+p_{yy}) &= \gamma\, n_x n_y\,[\tilde{\eta}_1 + \tfrac{1}{2}\eta_{12}(1-3n_z^2)]\end{aligned}$$

and

$$\tfrac{1}{3}p_{\lambda\lambda} = -\varkappa\gamma\, n_x n_y, \tag{25}$$

where $n_{x,y,z}$ are the components of $\boldsymbol{n}$ with respect to the coordinate axes. The quantities (24, 25) vanish for the orientations "1, 2, 3" of the director $\boldsymbol{n}$. The existence of the "transverse" pressure $p_{xx} - p_{yy}$ has been demonstrated experimentally [18], the other quantities have not yet been measured.

1.4. Flow Alignment and Viscosity for a Free Flow

The antisymmetric part of the pressure tensor is associated with a torque density by

$$\vartheta_\mu = -\varepsilon_{\mu\nu\lambda}\, p_{\nu\lambda} = -\varepsilon_{\mu\nu\lambda}\, p^{\mathrm{a}}_{\nu\lambda}. \tag{26}$$

For a stationary flow and without orienting external fields, ϑ_μ and $p^{\mathrm{a}}_{\nu\mu}$ vanish. For the plane Couette geometry considered above, (26) and (11) imply that the director lies in the shear plane and encloses the angle ϕ_0 (flow alignment angle) with the x-direction:

$$\boldsymbol{n} = \cos\phi_0\, \boldsymbol{e}^x + \sin\phi_0\, \boldsymbol{e}^y.$$

Subject to the condition $|\gamma_2| > \gamma_1$, ϕ_0 is given by

$$\cos 2\phi_0 = -\gamma_1/\gamma_2. \tag{27}$$

In this case the viscosity of a freely flowing (flow aligned) nematic liquid crystal becomes

$$\begin{aligned}\eta_S &= \tfrac{1}{2}(\eta_1+\eta_2-\gamma_1) + \tfrac{1}{4}\eta_{12}\,[1-(\gamma_1/\gamma_2)^2]\\ &= \eta + \tfrac{1}{6}\tilde{\eta}_1 - \tfrac{1}{4}\gamma_1 + \tfrac{1}{2}\tilde{\eta}_3\,[1-(\gamma_1/\gamma_2)^2].\end{aligned} \tag{28}$$

Measurements of γ_1 and η_S for a large class of nematic liquid crystals were reported in [19]. The equation $\boldsymbol{\vartheta} = 0$, cf. (26), has also the solution $\boldsymbol{n} = \boldsymbol{e}^z$. In this case the viscosity would by equal to η_3. This type of flow orientation, however, is instable, in general. Positive entropy production implies $\gamma_1 > 0$ and $\eta_i > 0$, $i = 1, 2, 3$; however γ_2, η_{12} and $\varkappa$ may have either sign.

2. Affine Transformation Model for Perfectly Oriented Molecules

2.1. Definition of the Model

The pressure tensor of a fluid is a sum of "kinetic" and "potential" contributions:

$$P_{\nu\mu} = P^{\mathrm{kin}}_{\nu\mu} + P^{\mathrm{pot}}_{\nu\mu}; \tag{29}$$

the latter contribution is the dominating one for dense fluids. Microscopic expressions for these quantities are

$$V\, P^{\mathrm{kin}}_{\nu\mu} = \sum_i m\, c^i_\nu\, c^i_\mu \tag{30}$$

and

$$V\, P^{\mathrm{pot}}_{\nu\mu} = \sum_i r^i_\nu\, F^i_\mu = -\sum_i r^i_\nu\, \frac{\partial \Phi^{(N)}}{\partial r^i_\mu}. \tag{31}$$

Here $i = 1, 2, \ldots, N$ labels the molecules with mass m contained in a volume V; $\boldsymbol{r}^i$ and $\boldsymbol{c}^i$ are the positions (of the center of mass) and peculiar velocities of the particles. It is understood that there is no external force included in F^i_μ, i.e. one has $\sum_i F^i_\mu = 0$. The quantity $\Phi^{(N)}$ is the N-particle potential which is given as a sum of binary interactions,

$$\Phi^{(N)} = \tfrac{1}{2}\sum_{i \neq j}\sum \Phi_{\mathrm{A}}(\boldsymbol{r}^{ij}) \tag{32}$$

with $\boldsymbol{r}^{ij} = \boldsymbol{r}^i - \boldsymbol{r}^j$.

Now it is assumed that the nonspherical potential $\Phi_{\mathrm{A}} = \Phi_{\mathrm{A}}(\boldsymbol{r})$ is obtained from a spherical interaction potential $\Phi(\boldsymbol{r}^{\mathrm{A}})$ by an affine transformation:

$$\Phi_{\mathrm{A}}(\boldsymbol{r}) = \Phi(\boldsymbol{r}^{\mathrm{A}}) \tag{33}$$

with $\boldsymbol{r}$ and $\boldsymbol{r}^{\mathrm{A}}$ linked by

$$r_\mu^{\mathrm{A}} r_\mu^{\mathrm{A}} = r_\mu A_{\mu\nu} r_\nu \tag{34}$$

or

$$r_\mu^{\mathrm{A}} = A_{\mu\nu}^{1/2} r_\nu . \tag{35}$$

The transformation matrix $A_{\mu\nu}$ with positive eigenvalues describes the mapping of a sphere $\boldsymbol{r}^{\mathrm{A}} \cdot \boldsymbol{r}^{\mathrm{A}} = \text{const}$ on an ellipsoid. In (33), $\boldsymbol{r}$ stands for the difference $\boldsymbol{r}^{ij} = \boldsymbol{r}^i - \boldsymbol{r}^j$ between the position vectors of two particles. Since all molecules are assumed to be perfectly oriented in the same direction, the same transformation (35) can be used for all coordinates. This means that the fluid of oriented nonspherical particles is affinely related to a fluid of spherical ones. It is convenient to use a volume conserving mapping where the eigenvalues A_i, $i = 1, 2, 3$, of $A_{\mu\nu}$ obey the relation

$$A_1 A_2 A_3 = 1 . \tag{36}$$

Then the spherical equipotential surface of $\Phi(\boldsymbol{r}^{\mathrm{A}})$ encloses the same volume as the corresponding elliptical potential surface of $\Phi_{\mathrm{A}}(\boldsymbol{r})$. Next, it is demonstrated that some general conclusions can be drawn from the assumptions made so far without introducing a specific functional form (such as hard or soft spheres or Lennard-Jones interaction) for $\Phi(\boldsymbol{r}^{\mathrm{A}})$. the explicit form of the transformation matrix $A_{\mu\nu}$ is presented later for the special case of ellipsoids of revolution.

In the following we restrict our attention to the (dominating) potential contribution to the pressure tensor.

2.2. *Potential Contribution to the Pressure Tensor*

Due to (35), the spatial derivative $\partial/\partial r_\mu = \nabla_\mu$ is linked with ∇_μ^{A} in the affine space by

$$\nabla_\mu^{\mathrm{A}} = A_{\mu\nu}^{-1/2} \nabla_\nu . \tag{37}$$

Thus one has

$$P_{\mu\nu}^{\mathrm{pot,\,A}} = A_{\mu\lambda}^{1/2} P_{\lambda\varkappa}^{\mathrm{pot}} A_{\varkappa\nu}^{-1/2} \tag{38}$$

for the relation between the potential contribution to the pressure tensor in real and in the affine space. In thermal equilibrium one has $P_{\nu\mu}^{\mathrm{pot,\,A}} = P_{\mathrm{A}}^{\mathrm{pot}} \delta_{\nu\mu}$; (38) then implies $P_{\nu\mu}^{\mathrm{pot}} = P_{\mathrm{A}}^{\mathrm{pot}} \delta_{\nu\mu}$, i.e. the pressure tensor of the fluid of non-isotropic particles is also isotropic in equilibrium.

The eq. (38) also applies to the potential contribution to the friction pressure tensor $p_{\nu\mu}$ (cf. (2)) which is assumed to be determined by the standard ansatz for an isotropic fluid in the affine space:

$$-p_{\mu\nu}^{\mathrm{pot,\,A}} = \alpha_4^{\mathrm{pot,\,A}} \gamma_{\mu\nu}^{\mathrm{A}} + \eta_{\mathrm{V}}^{\mathrm{A}} \nabla_\lambda^{\mathrm{A}} v_\lambda^{\mathrm{A}} \delta_{\mu\nu} . \tag{39}$$

Notice that $\nabla_\lambda^{\mathrm{A}} v_\lambda^{\mathrm{A}} = \nabla_\lambda v_\lambda$ and the symmetric traceless deformation rate tensor $\gamma_{\nu\mu}^{\mathrm{A}}$ is related to the velocity gradient in real space by

$$\gamma_{\mu\nu}^{\mathrm{A}} = \tfrac{1}{2}(A_{\mu\lambda}^{-1/2} A_{\nu\varkappa}^{1/2} + A_{\nu\lambda}^{-1/2} A_{\mu\varkappa}^{1/2}) \nabla_\lambda v_\varkappa - \tfrac{1}{3} \nabla_\lambda v_\lambda \delta_{\mu\nu} . \tag{40}$$

Now use of (38) with (39, 40) leads to

$$-p_{\mu\nu}^{\mathrm{pot}} = \alpha_4^{\mathrm{pot,\,A}} [\tfrac{1}{2} (A_{\mu\lambda}^{-1} \nabla_\lambda v_\varkappa A_{\varkappa\nu} + \nabla_\nu v_\mu) - \tfrac{1}{3} \nabla_\lambda v_\lambda \delta_{\mu\nu}] + \eta_{\mathrm{V}}^{\mathrm{A}} \nabla_\lambda v_\lambda \delta_{\mu\nu} . \tag{41}$$

This means that the potential contributions to the seven independent viscosity coefficients of (9–12) can be expressed in terms of the coefficients $\alpha_4^{\mathrm{pot,\,A}}$ and $\eta_{\mathrm{V}}^{\mathrm{A}}$ and the properties of the affine transformation matrix $A_{\mu\nu}$ which contains the information on the direction of the orientation of the molecules and on their "non-sphericity".

2.3. *Ellipsoids of Revolution*

For ellipsoids of revolution with their figure axis parallel to the unit vector $\boldsymbol{u}$ one has

$$A_{\mu\nu} = [(1 - \tfrac{1}{3} A)^2 (1 + \tfrac{2}{3} A)]^{-1/3} (\delta_{\mu\nu} + A \,\overline{u_\mu u_\nu}), \tag{42}$$

where A with $-3/2 < A < 3$ is a nonsphericity parameter. The factor in the bracket guarantees the property (36). The equation (34) with $\boldsymbol{r}^{\mathrm{A}} \cdot \boldsymbol{r}^{\mathrm{A}} = \text{const}$ describes an ellipsoid with the semiaxes

$$a = [(1 - \tfrac{1}{3} A)(1 + \tfrac{2}{3} A)^{-1}]^{1/3} r_{\mathrm{A}}$$

and

$$b = c = [(1 + \tfrac{2}{3} A)(1 - \tfrac{1}{3} A)^{-1}]^{1/6} r_{\mathrm{A}} . \tag{43}$$

Thus the axes ratio is

$$Q = \tfrac{a}{b} = [(1 - \tfrac{1}{3} A)(1 + \tfrac{2}{3} A)^{-1}]^{1/2}, \tag{44}$$

and one has

$$A = 3(1 - Q^2)(1 + 2Q^2)^{-1} . \tag{45}$$

Prolate and oblate particles correspond to $Q > 1$, $A < 0$ and $Q < 1$, $A > 0$, respectively. For spherical particles, i.e. for $Q = 1$, $A = 0$, (42) reduces to $A_{\mu\nu} = \delta_{\mu\nu}$. In general, the transformation matrix can also be written as

$$A_{\mu\nu} = Q^{2/3} [\delta_{\mu\nu} + (Q^{-2} - 1) u_\mu u_\nu], \tag{46}$$

and its inverse is given by

$$A^{-1}_{\mu\nu} = Q^{-2/3}\,[\delta_{\mu\nu} + (Q^2 - 1)\,u_\mu u_\nu]. \tag{47}$$

Insertion of (46, 47) into (41), use of $\boldsymbol{u} = \boldsymbol{n}$ (complete alignment) and comparison with the ansatz (9) now yields for the potential contributions to the viscosity coefficients:

$$\begin{aligned}
\alpha_4^{\text{pot}} &= \alpha_4^{\text{pot, A}},\\
\alpha_1^{\text{pot}} &= -\tfrac{1}{2}(Q - Q^{-1})^2\,\alpha_4^{\text{pot}}, \qquad (48)\\
\alpha_2^{\text{pot}} &= \tfrac{1}{2}(1 - Q^2)\,\alpha_4^{\text{pot}},\\
\alpha_3^{\text{pot}} &= \tfrac{1}{2}(Q^{-2} - 1)\,\alpha_4^{\text{pot}},\\
\alpha_5^{\text{pot}} &= \tfrac{1}{2}(Q^2 - 1)\,\alpha_4^{\text{pot}} = -\,\alpha_2^{\text{pot}},\\
\alpha_6^{\text{pot}} &= \tfrac{1}{2}(Q^{-2} - 1)\,\alpha_4^{\text{pot}} = \alpha_3^{\text{pot}}, \qquad (49)\\
\eta_{\text{V}} &= \eta_{\text{V}}^{\text{A}},\\
\varkappa^{\text{pot}} &= \zeta_2^{\text{pot}} = 0. \qquad (50)
\end{aligned}$$

With $\alpha_4^{\text{pot, A}} = 2\,\eta_{\text{iso}}^{\text{pot}}$, where the subscript "iso" refers to the affine "isotropic" fluid, (48–50) are equivalent to (cf. (14, 15))

$$\begin{aligned}
\eta^{\text{pot}} &= [1 + \tfrac{1}{6}(Q - Q^{-1})^2]\,\eta_{\text{iso}}^{\text{pot}},\\
\tilde{\eta}_1^{\text{pot}} &= \tfrac{1}{2}(Q - Q^{-1})^2\,\eta_{\text{iso}}^{\text{pot}},\\
\tilde{\eta}_2^{\text{pot}} &= \tfrac{1}{2}(Q^{-2} - Q^2)\,\eta_{\text{iso}}^{\text{pot}},\\
\tilde{\eta}_3^{\text{pot}} &= -\,\tfrac{1}{2}(Q - Q^{-1})^2\,\eta_{\text{iso}}^{\text{pot}}, \qquad (51)
\end{aligned}$$

and

$$\begin{aligned}
\gamma_1 &= (Q - Q^{-1})^2\,\eta_{\text{iso}}^{\text{pot}},\\
\gamma_2 &= (Q^{-2} - Q^2)\,\eta_{\text{iso}}^{\text{pot}}. \qquad (52)
\end{aligned}$$

Notice that the kinetic part of the pressure tensor is symmetric. Consequently, the coefficients γ_1 and γ_2 – and by the Onsager symmetry relation (17) also $\tilde{\eta}_2$ – are completely determined by the potential contributions listed above; the coefficients η, $\tilde{\eta}_1$ and $\tilde{\eta}_3$ possess kinetic contributions, in general. From (51, 52) follows

$$2\,\tilde{\eta}_1^{\text{pot}} = \gamma_1, \tag{53}$$

which appears to be analogous to (17) but is not as general as the Onsager symmetry relation. The potential contributions to the Miesowicz viscosities, cf. (21–23), for the present model are

$$\begin{aligned}
\eta_3^{\text{pot}} &= \eta_{\text{iso}}^{\text{pot}},\\
\eta_1^{\text{pot}} &= Q^{-2}\,\eta_3^{\text{pot}},\\
\eta_2^{\text{pot}} &= Q^2\,\eta_3^{\text{pot}}, \qquad (54)
\end{aligned}$$

and

$$\eta_{12}^{\text{pot}} = -\,(Q - Q^{-1})^2\,\eta_3^{\text{pot}} = -\,\gamma_1. \tag{55}$$

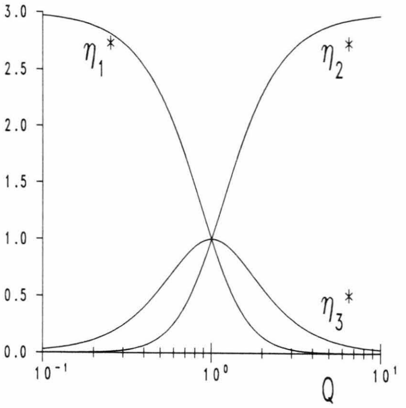

Fig. 1. The Miesowicz viscosity coefficients η_i, $i = 1, 2, 3$ in units of the average viscosity $\bar{\eta} = \frac{1}{3}(\eta_1 + \eta_2 + \eta_3)$ as functions of the axes ratio Q for prolate $(Q > 1)$ and oblate $(Q < 1)$ particles. Notice that a logarithmic scale is used for Q.

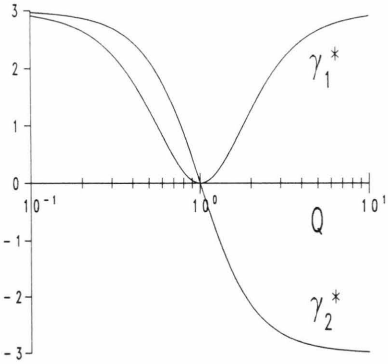

Fig. 2. The Leslie coefficients γ_1 and γ_2 in units of $\bar{\eta}$ as functions of the axis ratio Q. Notice that $\gamma_2 < 0$ for $Q > 1$ and $\gamma_2 > 0$ for $Q < 1$.

The ratios $\eta_1^{\text{pot}}/\eta_2^{\text{pot}} = Q^{-4}$ and $\frac{1}{2}(\gamma_1 - \gamma_2)/\eta_2^{\text{pot}} = 1 - Q^{-2}$ agree with results derived by Helfrich [14] for $Q > 1$. In Fig. 1, the (reduced) Miesowicz viscosities η_i, $i = 1, 2, 3$, in units of the average viscosity $\bar{\eta} = \frac{1}{3}(\eta_1 + \eta_2 + \eta_3)$ are plotted as functions of the axes ratio Q. Notice that $\eta_2 > \eta_3 > \eta_1$ for prolate particles $(Q > 1)$ and $\eta_1 > \eta_3 > \eta_2$ for oblate particles $(Q < 1)$. Similarly, in Fig. 2, γ_1 and γ_2 (in units of $\bar{\eta}$) are displayed as functions of Q. Both γ_1 and γ_2 vanish for spherical particles $(Q = 1)$. Notice that $\gamma_2 < 0$ for $Q > 1$ and $\gamma_2 > 0$ for $Q < 1$. The scaled coefficients are denoted by η_i^* and γ_i^*.

The flow alignment angle which follows from γ_1, γ_2 given above is

$$\phi_0 = \tfrac{1}{2}\,[\pi + \text{sign}\,(A\,\gamma)\,\arccos\,[(1 - Q^2)(1 + Q^2)^{-1}]], \tag{56}$$

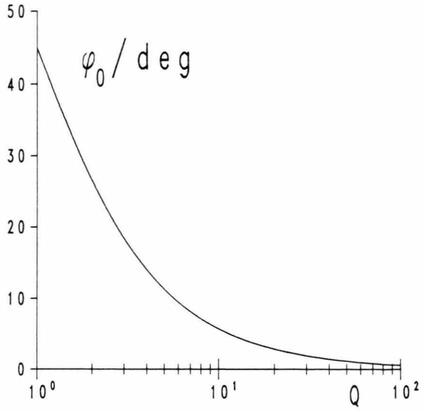

Fig. 3. The flow alignment angle ϕ_0 as function of Q for prolate particles ($Q > 1$).

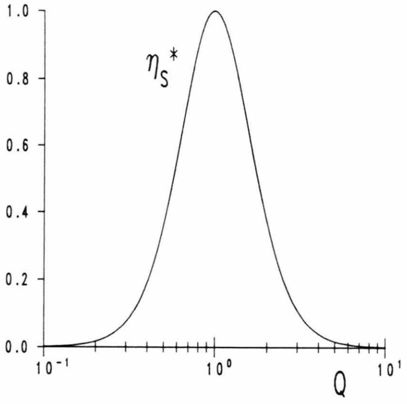

Fig. 4. The viscosity η_S for a free flow in units of $\bar{\eta}$ as function of the axis ratio Q.

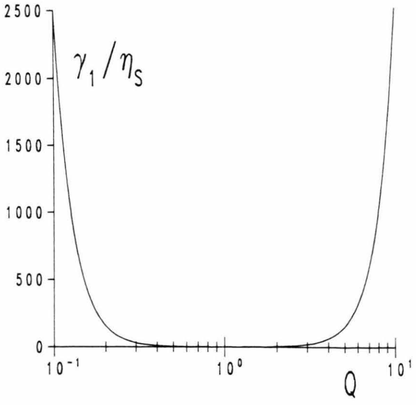

Fig. 5. The ratio between the Leslie coefficient γ_1 and the viscosity η_S for a free flow as function of the axis ratio Q.

where γ is the shear rate and $A < 0$ for prolate particles. For this case, ϕ_0 is shown in Figure 3. The potential contribution to the viscosity for a free flow (no orienting external fields), cf. (28), is

$$\eta_S^{\text{pot}} = 4(Q + Q^{-1})^{-2}\,\eta_3^{\text{pot}} = 4\,[(\eta_1^{\text{pot}})^{-1} + (\eta_2^{\text{pot}})^{-1} + 2(\eta_3^{\text{pot}})^{-1}]^{-1}. \tag{57}$$

Notice that $\eta_S^{\text{pot}} < \eta_{\text{iso}}^{\text{pot}}$. The ratios $\eta_S/\bar{\eta}$ and γ_1/η_S as functions of Q are shown in Figs. 4 and 5, respectively.

2.4. Remarks on the Kinetic Contribution to the Pressure Tensor and on the Validity of (39, 41)

It seems tempting to use arguments similar to those which led to (39) in order to calculate the kinetic contribution to the friction pressure. From $c_\mu = A_{\mu\nu}^{-1/2}\,c_\nu^{\text{A}}$, where $\boldsymbol{c}^{\text{A}}$ is the velocity in the affinely deformed space, one would obtain

$$c_\mu c_\mu = c_\mu^{\text{A}}\,A_{\mu\nu}^{-1}\,c_\nu^{\text{A}}, \tag{58}$$

which would imply that – in the affine space – the velocity distribution function is already anisotropic in equilibrium. Thus well-known relations from isotropic fluids cannot be used for the kinetic contribution to the friction pressure tensor. Here, it is simply disregarded because it is much smaller than the potential contribution. At the same time, it becomes evident that relation (39) is not as general as it seemed at first glance. The underlying assumption becomes more apparent if the N-particle average (31) is replaced by the integral over the pair-correlation function $g_{\text{A}}(\boldsymbol{r})$,

$$P_{\nu\mu}^{\text{pot}} = -\tfrac{1}{2}\,n^2 \int r_\nu \frac{\partial \Phi_{\text{A}}}{\partial r_\mu}\,g_{\text{A}}(\boldsymbol{r})\,\mathrm{d}^3 r, \tag{59}$$

where $n = N/V$ is the number density and $\Phi_{\text{A}} = \Phi_{\text{A}}(\boldsymbol{r}) = \Phi(r_{\text{A}})$ is the binary interaction potential. Relations (39) and (41) are equivalent to the assumption that the pair-correlation function $g_{\text{A}}(\boldsymbol{r})$ of the oriented nonspherical particles (in analogy to (33)) is equal to the pair-correlation function $g(\boldsymbol{r})$ of a fluid of spherical particles related to the original ones by the affine transformation (35). Such an interrelation has previously been conjectured for the equilibrium structure of oriented nematic liquid crystals [20]; here it is extended to nonequilibrium properties.

Molecular dynamics simulations confirm that the consequences based on (39) and (41) are rather well obeyed [15, 16]; see also the Section 3.

2.5. *Non-Newtonian Viscosity*

So far, our considerations were restricted to the Newtonian viscosity. Assuming that (41) still applies in the non-Newtonian regime and observing the transformation behavior of the shear rate, we obtain the nonlinear generalizations of (54):

$$\begin{aligned} \eta_3^{\text{pot}}(\gamma) &= \eta_{\text{iso}}^{\text{pot}}(\gamma), \\ \eta_1^{\text{pot}}(\gamma) &= Q^{-2}\,\eta_3^{\text{pot}}(Q^{-1}\gamma), \\ \eta_2^{\text{pot}}(\gamma) &= Q^{2}\,\eta_3^{\text{pot}}(Q\,\gamma). \end{aligned} \tag{60}$$

Thus in liquid crystals with strongly anisotropic molecules nonlinear effects like shear thinning can occur at relatively smaller velocity gradients if the director lies along the direction of the gradient (flow velocity) for prolate (oblate) particles. This is indeed observed in NEMD computer simulations [15, 16]. For the coefficients γ_1 and γ_2 expressions analogous to (60) are

$$\begin{aligned} \tfrac{1}{2}(\gamma_1+\gamma_2) &= (Q^{-2}-1)\,\eta_3^{\text{pot}}(Q^{-1}\gamma), \\ \tfrac{1}{2}(\gamma_1-\gamma_2) &= (Q^{2}-1)\,\eta_3^{\text{pot}}(Q\gamma). \end{aligned} \tag{61}$$

3. Comparison of Analytical Calculation with Molecular-Dynamics Simulations and Experimental Data

3.1. *Nonequilibrium Molecular-Dynamics Simulations for Ellipsoid Potentials and Comparison to Theoretical Relations*

With a CDC Cyber 173 and a Cyber 845 at Erlangen as well as a Cray-1M and a Cray-XMP-24 at Berlin, we have performed NEMD simulations for a system of 128 particles interacting via a soft or a Lennard-Jones ellipsoid potential [15, 16]:

$$\Phi_{\text{SE}}(r_{\text{A}}) = r_{\text{A}}^{-12}, \tag{62}$$

$$\Phi_{\text{LJE}}(r_{\text{A}}) = 4(r_{\text{A}}^{-12} - r_{\text{A}}^{-6}). \tag{63}$$

The particles are rigidly oriented in the direction of a coordinate axis or of the bisector between the 1- and 2-axis. The system is subject to a plane couette flow (19). After computation of the kinetic and potential contributions to the pressure tensor $P_{\nu\mu}$ for different shear rates γ, we determine the Newtonian shear viscosity by an extrapolation to $\gamma = 0$:

$$\eta_i = -\lim_{\gamma\to 0} p_{yx}(\gamma)/\gamma, \quad i = 1, 2, 3, 45. \tag{64}$$

Table 1. NEMD results for the potential viscosity coefficients of SE and LJE fluids at number density n and temperature T.

	SE potential $n = 0.6$ $T = 0.25$	LJE potential $n = 0.6$ $T = 1.15$
	$Q = 7/3$ (prolate particles)	
η_1	0.09 ± 0.03	0.15 ± 0.04
η_2	2.8 ± 0.2	3.5 ± 0.3
η_3	0.52 ± 0.10	0.70 ± 0.10
η_{12}	-1.8 ± 0.3	-2.1 ± 0.4
γ_1	1.9 ± 0.3	2.2 ± 0.4
γ_2	-2.7 ± 0.3	-3.5 ± 0.4
$\varkappa$	0.0 ± 0.3	0.0 ± 0.4
	$Q = 1$ (spherical particles)	
η_{iso}	0.52 ± 0.10	0.73 ± 0.10

Table 2. Comparison between our theoretical relations and the NEMD results from Table 1.

	Theory	NEMD	
		SE	LJE
η_3/η_1	5.44	5.8 ± 0.4	4.7 ± 0.5
η_2/η_3	5.44	5.4 ± 0.4	5.0 ± 0.5
η_{12}/γ_1	-1.00	-0.9 ± 0.4	-1.0 ± 0.4
η_3/η_{iso}	1.00	1.0 ± 0.2	1.0 ± 0.2
$\varkappa$	0.00	0.0 ± 0.3	0.0 ± 0.4

For the used type of interaction, the rotational viscosity is exactly given by

$$\gamma_1 = (1 - Q^2)\,\eta_1^{\text{pot}} + (1 - Q^{-2})\,\eta_2^{\text{pot}}. \tag{65}$$

The coefficients γ_1 and γ_2 can also be inferred from the antisymmetric part $\tfrac{1}{2}(p_{yx} - p_{xy})$ of the pressure tensor as computed in the NEMD simulation. If p_0 denotes the scalar friction pressure, we obtain the coefficient $\varkappa$ from a run with 45°-orientation according to

$$\varkappa = -2 \lim_{\gamma\to 0} p_0(\gamma)/\gamma. \tag{66}$$

It should be noted that the 45°-alignment and *one* of the three others already yield all desired coefficients. This is due to the fact that under 45° two normal pressure differences occur, cf. (24), which are related to the shear viscosities. However, it seems useful to have some redundant information in order to check the consistency of our calculations. In Tables 1 and 2, we present our NEMD results (in standard reduced units)

Table 3. Theoretical results (potential contributions) and LJE-NEMD data for 5 reduced viscosity coefficients are compared with the corresponding experimental values for 3 substances.

	η_1^*	η_2^*	η_3^*	η_{12}^*	γ_1^*
Theory (pot)	0.08	2.46	0.45	−1.64	1.64
LJE	0.15	2.33	0.52	−1.12	1.40
	±0.07	±0.3	±0.1	±0.4	±0.2
EM (40 °C)	0.37	2.07	0.57	–	1.62
MBBA (30 °C)	0.38	1.99	0.63	−0.28	1.55
N4 (50 °C)	0.32	2.14	0.54	−0.68	1.75
N4 ((33 ± 1) °C)	0.34	2.00	0.66	−1.21	2.00

for prolate and spherical particles as well as a comparison to the theoretic values, respectively. The index "pot" is omitted in both tables.

Within the accuracy of computation and extrapolation, we ascertain a good agreement between theory and computer experiment.

3.2. Comparison to Experimental Data for Real Nematics

There exist precise measurements of the shear and rotational viscosities of different nematic liquid crystals by Kneppe, Schneider, and Sharma [2–4]. In Table 3, our theoretical and numerical values for 5 viscosity coefficients in units of the average shear viscosity $\bar{\eta} = \frac{1}{3}(\eta_1 + \eta_2 + \eta_3)$ are compared with some of these experimental data. For η_1, η_2, η_3 and γ_1 this comparison has already been made previously [15]. In the last line data inferred from tables and graphs in [21] for N4 are listed. The value of η_{12} for N4 at 50 °C has also been taken from [21]. The scaled viscosity coefficients $\eta_i/\bar{\eta}$ and $\gamma_i/\bar{\eta}$ are denoted by η_i^* and γ_i^*.

In this comparison between theory and the experimental data one should keep in mind that the theoretical values apply to a perfectly aligned fluid (Maier-Saupe order parameter $S = 1$) of particles with an axes ratio Q (where the special value $Q = 7/3$ was chosen) whereas the real fluids are only partially ordered ($0.4 \lesssim S \lesssim 0.8$) but they consist of molecules with a larger axis ratio Q_m. For a more quantitative comparison, an expression for the effective axis ratio Q of the perfectly aligned model fluid in terms of S and Q_m of the real liquid crystal is still needed. For temperatures well within the nematic range $Q = S\,Q_m$ seems to be a likely guess. For η_2, η_3, and γ_1, the comparison between the theoretical and experimental values is quite satisfactory; for η_1 and the magnitude of η_{12} one observes larger discrepancies. The essential qualitative features, however such as $\eta_2 > \eta_3 > \eta_1$, $\gamma_2 < 0$, $\eta_{12} < 0$, for nematics are well described by the theoretical model.

4. Concluding Remarks

In this article, it has been demonstrated how the 7 independent viscosity coefficients of a nematic or nematic discotic liquid crystal can be expressed in terms of the shear viscosity and the bulk viscosity of a reference fluid of spherical particles and the axes ratio Q of the ellipsoidal particles. Apart from the fixed orientation (perfect alignment) the crucial point is the use of a nonspherical interaction potential obtained from a spherical one by an affine transformation which characterizes the anisotropy of the "shape" of a molecule. This, on the one hand, allows the derivation of rather general exact relations which are confirmed by nonequilibrium molecular dynamics simulations. On the other hand, in a comparison with real nematic liquid crystal one should bear in mind that dipole-dipole and quadrupole-quadrupole interactions were not taken into account in the present treatment. The fact that the magnitude of the theoretical value for the coefficient η_{12} is too large when compared with experimental data may be associated with this point. The comparison of theoretical and experimental values for the Miesowicz viscosities η_1, η_2, η_3 and the Leslie coefficients γ_1, γ_2, however, indicates that the affine transformation model contains the essential features for the explanation of the anisotropy of the viscosity of nematic and nematic discotic liquid crystals.

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