Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Viscosities of Nematic and Discotic Nematic Liquid Crystals According to the Affine Transformation Model

Martin Kröger [a] & Shaun Sellers [b]

[a] Institut für Theoretische Physik, Technische Universität Betlin, D-10623, Berlin, Germany

[b] Dipartimento di Ingegneria Civile, Università di Roma “Tor Vergata,”, 1-00133, Roma, Italy

Version of record first published: 04 Oct 2006

To cite this article: Martin Kröger & Shaun Sellers (1997): Viscosities of Nematic and Discotic Nematic Liquid Crystals According to the Affine Transformation Model, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 300:1, 245-262

To link to this article: http://dx.doi.org/10.1080/10587259708042351

Mol. Cryst. Liq. Cryst., 1997, Vol. 300, pp. 245–262
Reprints available directly from the publisher
Photocopying permitted by license only

Viscosities of Nematic and Discotic Nematic Liquid Crystals According to the Affine Transformation Model

MARTIN KRÖGER[a] and SHAUN SELLERS[b]

[a]*Institut für Theoretische Physik, Technische Universität Berlin,*
D-10623 Berlin, Germany;
[b]*Dipartimento di Ingegneria Civile, Università di Roma "Tor Vergata,"*
I-00133 Roma, Italy

(Received 22 October 1996; In final form 11 February 1997)

An affine transformation model is used to calculate the macroscopic stress tensor for uniaxial liquid crystals. In the special case of constant degrees of alignment, it is shown to be of the form occurring in the Ericksen-Leslie director theory for nematic liquid crystals, resolving an apparent discrepancy on the form of the stress tensor. The corresponding Leslie and Miesowicz viscosities are calculated in terms of the alignment order parameters and those of the affine model. These results improve the approximate calculations of Ehrentraut and Hess [*Phys. Rev. E* **51**, 2203 (1995)] based on a hindered rotation assumption. It is further shown that the calculated orientation-dependence of the viscosities based on the affine model is the same as that resulting from calculations based on an alternative Fokker-Planck equation for the one particle orientational distribution function.

Keywords: Liquid crystal theory; nematics; discotics; rheology; affine transformation

INTRODUCTION

The anisotropy of liquid crystals leads to numerous viscosity coefficients in order to describe the flow properties. Recently there has been some interest in calculating these viscosities. A common approach uses statistical models [1–15] based on a Fokker-Planck equation approach introduced by Hess [16] and Doi [17]. The method relates the viscosities to the particle geometry and the alignment order parameters. An alternative procedure for modelling nematic liquid crystals is based on the affine transformation model [18–20], which was proposed to describe anisotropic fluids consisting of perfectly aligned ellipsoidal particles. It uses an affine variable transformation to relate the physical properties of a perfectly aligned anisotropic fluid to those of a linearly viscous isotropic fluid. This model has also been extended to biaxial particles [21].

Various non-equilibrium molecular dynamics simulations [19, 20, 22, 23] of perfectly aligned fluids have supported the predictions of the affine transformation model. Real liquid crystals however are not perfectly aligned, so that comparison to experimental data is difficult. Motivated by the success of a generalization of the affine transformation model to describe diffusion in partially aligned fluids [24], the same procedure to obtain the stress tensor for partially aligned fluids was applied recently in Refs. [25, 26]. Upon comparing the resulting stress tensor with the stress tensor in the Ericksen-Leslie continuum theory [27–29], they obtained relations for the Leslie viscosities in terms of the particle geometry and alignment order parameters. In these calculations, however, they assumed some restrictive mathematical simplications: hindered particle rotations and, hence, steady-state director solutions. While for certain flow conditions or certain fluids such assumptions may be valid, they do not hold in general. For example, it is well known that for some materials the director undergoes periodic tumbling motion in steady shear. Furthermore a rotational viscosity tensor was obtained (instead of the usual scalar rotational viscosity). They obtained thus only partial agreement with the Ericksen-Leslie theory, Such a result would seem to us to question the general validity of the approximations made.

As in [25, 26], we present here a calculation of the viscosities according to the modified affine transformation model. Our point of departure is the method of calculating the viscosities, which does not involve the hindered rotation assumption. Our approach leads to viscosity expressions that differ somewhat from those given in [25, 26]. In particular we show that if the order parameters are constant, then the correspondence with the Ericksen-Leslie stress tensor is exact. Furthermore we obtain explicit relations for all the Leslie viscosities. While the expressions for the remaining Leslie viscosities Refs. [25, 26] remain unchanged, their expressions for the Miesowicz viscosities must be corrected. Sample numerical calculations are given to illustrate the differences. For simplicity we treat only incompressible fluids. The results for compressible fluids (as treated in Ref. [26]) follow in a straightforward manner.

A comparison is made with alternative calculations based on a Fokker-Planck equation [12]. It is shown that there is a surprising similarity in the two approaches in that they both predict the same type of dependence of the viscosities on the alignment order parameters, although the dependence on the particle geometry differs. Experimental data however does not seem sufficient to discern between the two models.

I. PHENOMENOLOGY

A. Ericksen-Leslie Stress

It is common to use the Ericksen-Leslie theory [27–29] as a model for the flow properties of liquid crystals. Here we fix notation and cite the results that will be needed later.

In the Ericksen-Leslie theory, a unit vector **n** (the director) is introduced to represent the macroscopic symmetry axis at each point in space. The stress tensor $\boldsymbol{\sigma}$ is assumed to depend on the velocity gradients $\nabla \mathbf{v}$, the director **n**, and a corotational time derivative of the director **N**. For an incompressible nematic liquid crystal, the viscous stress tensor is given by:

$$\sigma_{\mu\nu} = \alpha_1 n_\lambda n_\kappa \Gamma_{\lambda\kappa} n_\mu n_\nu + \alpha_2 n_\mu N_\nu + \alpha_3 n_\nu n_\mu$$
$$+ \alpha_4 \Gamma_{\mu\nu} + \alpha_5 n_\mu n_\lambda \Gamma_{\lambda\nu} + \alpha_6 n_\nu n_\lambda \Gamma_{\lambda\mu}. \quad (1)$$

In the above,

$$\Gamma_{\mu\nu} \equiv \frac{1}{2}(\partial_\mu v_\nu + \partial_\nu v_\mu),$$

$$\Omega_{\mu\nu} \equiv \frac{1}{2}(\partial_\mu v_\nu - \partial_\nu v_\mu),$$

$$N_\mu \equiv \dot{n}_\mu - \Omega_{\mu\lambda} n_\lambda. \quad (2)$$

As usual the isotropic terms have been incorporated into the pressure. In addition, it is usual to introduce the rotational viscosities γ_1 and γ_2 defined by

$$\gamma_1 \equiv \alpha_3 - \alpha_2, \quad \gamma_2 \equiv \alpha_6 - \alpha_5. \quad (3)$$

They appear in the equation for the director. Another common parameter is

$$\lambda \equiv -\frac{\gamma_2}{\gamma_1}, \tag{4}$$

which for $|\lambda| \geqslant 1$ is related to the flow alignment angle.

B. Miesowicz Viscosities

Commonly measured viscosities are the three Miesowicz viscosities [30] η_1, η_2, η_3. They are the effective viscosities in a plane shearing flow with the director aligned in the direction of one of the three unit axes. In terms of the Leslie viscosities they are given by

$$\eta_1 \equiv \frac{1}{2}(\alpha_3 + \alpha_4 + \alpha_6),$$

$$\eta_2 \equiv \frac{1}{2}(\alpha_4 + \alpha_5 - \alpha_2),$$

$$\eta_3 \equiv \frac{1}{2}\alpha_4. \tag{5}$$

An additional effective viscosity η_{12} has been introduced by Helfrich [31] for shearing flow. It is defined as

$$\eta_{12} \equiv \alpha_1. \tag{6}$$

C. Goal

Our goal in this paper is to calculate the viscosities $\alpha_i, \gamma_i, \lambda$, and η_i based on the affine transformation model for partially aligned liquid crystals (summarized in section 2) and to compare them with the corresponding results from a Fokker-Planck equation approach (summarized section 5).

II. AFFINE TRANSFORMATION MODEL

A. Perfect Alignment

In order to fix notation, we summarize here the basic results of the affine transformation model. More details can be found in the original papers

[19, 20]. The affine transformation model starts from a nonspherical interaction potential $\tilde{\Phi}(\mathbf{r})$ for ellipsoids of revolution which is obtained from a spherical interaction potential $\Phi(\tilde{r})$ with $\tilde{r} = \|\tilde{\mathbf{r}}\|$ by an affine transformation, $\tilde{\Phi}(\mathbf{r}) = (\tilde{\mathbf{r}})$, with $\mathbf{r}$ and $\tilde{\mathbf{r}}$ linked by

$$\tilde{r}_\mu = A_{\mu\nu}^{1/2} r_\nu. \tag{7}$$

A volume preserving transformation of a sphere into an ellipsoid of revolution of axis ratio Q ($Q > 1$ for rod-like particles, $Q < 1$ for disc-like particles) and axis of symmetry u is obtained for

$$A_{\mu\nu} \equiv Q^{2/3}[\delta_{\mu\nu} + (Q^{-2} - 1)u_\mu u_\nu]. \tag{8}$$

The microscopic expression for the potential contribution to the stress tensor σ is related to the two-body potential through the virial $\sigma_{\mu\nu} \propto \langle r_\mu \nabla_\nu \tilde{\Phi} \rangle$. Due to (7), the spatial derivative ∇ is linked with $\tilde{\nabla}$ in the affine space by $\tilde{\nabla}_\mu = A_{\mu\nu}^{-1/2} \nabla_\nu$. It follows that the strain rate tensors (as defined in 2) written in the different frames are related as

$$\tilde{\Gamma}_{\mu\nu} = \frac{\Gamma_{\lambda\kappa}}{2}(A_{\mu\lambda}^{-1/2} A_{\nu\kappa}^{-1/2} + A_{\nu\lambda}^{-1/2} A_{\mu\kappa}^{-1/2}). \tag{9}$$

Thus one has $\tilde{\sigma}_{\mu\nu} = A_{\mu\lambda}^{-1/2} \sigma_{\lambda\kappa} A_{\kappa\nu}^{-1/2}$. With the usual assumption for the viscous stress tensor of an incompressible isotropic fluid

$$\tilde{\sigma}_{\mu\nu} = 2\eta^{\text{ref}} \tilde{\Gamma}_{\mu\nu}, \tag{10}$$

the measurable viscous stress for the anisotropic fluid becomes (let us introduce the indexing $^{\text{ord}}$ in order to denote perfectly ordered)

$$\sigma_{\mu\nu}^{\text{ord}} = \eta^{\text{ref}}(A_{\mu\lambda}^{-1} \partial_\lambda v_\kappa A_{\kappa\nu} + \partial_\nu v_\mu). \tag{11}$$

Substituting (7) into (11) yields a stress tensor of the form

$$\begin{aligned} \sigma_{\mu\nu}^{\text{ord}} &= \alpha_1^{\text{ord}} u_\mu u_\nu u_\lambda u_\kappa \Gamma_{\lambda\kappa} + \alpha_2^{\text{ord}} u_\mu U_\nu \\ &\quad + \alpha_3^{\text{ord}} u_\nu U_\mu + \alpha_4^{\text{ord}} \Gamma_{\mu\nu} + \alpha_5^{\text{ord}} u_\mu u_\lambda \Gamma_{\lambda\nu} \\ &\quad + \alpha_6^{\text{ord}} u_\nu u_\lambda \Gamma_{\lambda\mu}. \end{aligned} \tag{12}$$

with $U_\mu \equiv \dot{u}_\mu - \Omega_{\mu\lambda} u_\lambda$. The coefficients of the perfectly aligned fluid are given by

$$\begin{aligned}
&\alpha_1^{\text{ord}} = -\eta^{\text{ref}}(Q - Q^{-1})^2, && \alpha_2^{\text{ord}} = \eta^{\text{ref}}(1 - Q^2),\\
&\alpha_3^{\text{ord}} = \eta^{\text{ref}}(Q^{-2} - 1), && \alpha_4^{\text{ord}} = 2\eta^{\text{ref}},\\
&\alpha_5^{\text{ord}} = -\alpha_2^{\text{ord}}, && \alpha_6^{\text{ord}} = \alpha_3^{\text{ord}},\\
&\gamma_1^{\text{ord}} = -\eta^{\text{ref}}(Q^{-1} - Q)^2, && \gamma_2^{\text{ord}} = \eta^{\text{ref}}(Q^{-2} - Q^2),\\
&\lambda^{\text{ord}} = \frac{Q^2 + 1}{Q^2 - 1}. && \qquad (13)
\end{aligned}$$

Thus in the case of perfectly aligned ellipsoids with symmetry axis **u**, we can identify the **u** with the director **n** in the Ericksen-Leslie theory. Note that axis ratio Q is the only adjustable parameter in the affine model.

The Miesowicz viscosities of the perfectly aligned fluid are obtained from (5) and (13) and are given by

$$\begin{aligned}
\eta_1^{\text{ord}} &= Q^{-2}\eta^{\text{ref}},\\
\eta_2^{\text{ord}} &= Q^2\eta^{\text{ref}},\\
\eta_3^{\text{ord}} &= \eta^{\text{ref}},\\
\eta_{12}^{\text{ord}} &= -(Q - Q^{-1})^2\eta^{\text{ref}}. \qquad (14)
\end{aligned}$$

These analytical expressions for the viscosities were successfully compared with molecular dynamics computer simulations for ellipsoidal potentials [20].

The antisymmetric part of the stress tensor (12) is

$$\begin{aligned}
\sigma_{\mu\nu}^{\text{ord}} - \sigma_{\nu\mu}^{\text{ord}} &= (\alpha_2^{\text{ord}} - \alpha_3^{\text{ord}})(\mu_\mu U_\nu - u_\nu U_\mu)\\
&\quad + (\alpha_5^{\text{ord}} - \alpha_6^{\text{ord}})(u_\mu u_\lambda \Gamma_{\lambda\nu} - u_\nu u_\lambda \Gamma_{\lambda\mu}). \qquad (15)
\end{aligned}$$

The antisymmetric part of the stress is balanced by the external couples. In particular, when the external couples vanish, the antisymmetric part also vanishes, and we obtain

$$U_\mu = \lambda^{\mathrm{ord}}(\delta_{\mu\kappa} - u_\mu u_\kappa)\Gamma_{\kappa\nu} u_\nu. \tag{16}$$

B. Partial Alignment

We follow [26] and assume that the stress tensor σ for the partially aligned fluid is obtained by averaging the stress tensor σ^{ord} for a perfectly aligned fluid over all orientations:

$$\begin{aligned}\sigma_{\mu\nu} &= \langle \sigma^{\mathrm{ord}}_{\mu\nu} \rangle \\ &= \alpha_1^{\mathrm{ord}} \langle u_\mu u_\nu u_\lambda u_\kappa \rangle \Gamma_{\lambda\kappa} + \alpha_2^{\mathrm{ord}} \langle u_\mu U_\nu \rangle \\ &\quad + \alpha_3^{\mathrm{ord}} \langle u_\mu U_\nu \rangle + \alpha_4^{\mathrm{ord}} \Gamma_{\mu\nu} + \alpha_5^{\mathrm{ord}} \langle u_\mu u_\lambda \rangle \Gamma_{\lambda\nu} \\ &\quad + \alpha_6^{\mathrm{ord}} \langle u_\mu u_\lambda \rangle \Gamma_{\lambda\nu}. \end{aligned} \tag{17}$$

Eq. [17] is supported by other approaches, cf. [13], and is consistent with other previous calculations.

Again, in the case of no applied external couples, the antisymmetric part of the stress tensor vanishes. In this case we obtain from (17)

$$\langle U_\mu u_\nu \rangle - \langle u_\mu U_\nu \rangle = \lambda^{\mathrm{ord}}(\Gamma_{\mu\lambda} \langle u_\lambda u_\nu \rangle - \langle u_\mu u_\lambda \rangle \Gamma_{\lambda\nu}). \tag{18}$$

Note however that now the particle symmetry axis **u** and the director **n** no longer coincide. In the next section, we show how they are related in the case of uniaxial symmetry.

III. UNIAXIAL ALIGNMENT

To calculate the viscosities, appropriate expressions for moments of alignment are needed. Here we collect the necessary expressions. In the case of uniaxial symmetry (**n** being the symmetry axis), the second and fourth moments of the alignment reduce to the following expressions [32]:

$$\langle u_\mu u_\nu \rangle = S_2 n_\nu n_\mu + \frac{1}{3}\delta_{\mu\nu}(1 - S_2), \tag{19}$$

$$
\begin{aligned}
\langle u_\mu u_\nu u_\lambda u_\kappa \rangle \Gamma_{\lambda\kappa} = {} & S_4 n_\mu n_\nu n_\lambda n_\kappa \Gamma_{\lambda\kappa} \\
& + \frac{2}{7}(S_2 - S_4)(n_\mu n_\lambda \Gamma_{\lambda\nu} + n_\nu n_\lambda \Gamma_{\lambda\mu}) \\
& + \frac{2}{15}\left(1 - \frac{10}{7} S_2 + \frac{3}{7} S_4\right)\Gamma_{\mu\nu} \\
& + \frac{1}{7}(S_2 - S_4)\delta_{\mu\nu} n_\lambda n_\kappa \Gamma_{\lambda\kappa}, \qquad (20)
\end{aligned}
$$

where the alignment order parameters are defined as averages of Legendre polynomials:

$$S_2 \equiv \langle P_2(\mathbf{u}\cdot\mathbf{n})\rangle, \quad S_4 \equiv \langle P_4(\mathbf{u}\cdot\mathbf{n})\rangle. \qquad (21)$$

They range in value by

$$-\frac{1}{2} \leqslant S_2 \leqslant 1, \quad -\frac{3}{7} \leqslant S_4 \leqslant 1. \qquad (22)$$

For perfect alignment $S_2 = S_4 = 1$; for random alignment (hence, isotropic) $S_2 = S_4 = 0$.

IV. VISCOSITIES FOR AFFINE TRANSFORMATION MODEL

A. Leslie Viscosities

We now proceed to the calculation of the viscosities. We neglect the explicit effect of the external couples on the viscosity coefficients, so that we may take the antisymmetric part of the stress as zero when calculating the viscosities. This assumption is supported by calculations based on a Fokker-Planck equation (see Sec. V) and is also consistent with those of [26]. Substitution of (19) and (20) into (17) and using (18) leads to the slightly more general expression for the stress tensor

$$
\begin{aligned}
\sigma_{\mu\nu} = {} & (\alpha_1 n_\lambda n_\kappa \Gamma_{\lambda\kappa} + \beta_1 S_2) n_\mu n_\nu \\
& + \alpha_2 n_\mu N_\nu + \alpha_3 n_\nu N_\mu \\
& + \alpha_4 \Gamma_{\mu\nu} + \alpha_5 n_\mu n_\lambda \Gamma_{\lambda\nu} + \alpha_6 n_\nu n_\lambda \Gamma_{\lambda\mu}, \qquad (23)
\end{aligned}
$$

where the coefficients are given by

$$\alpha_1 = S_4\alpha_1^{\mathrm{ord}} - \eta^{\mathrm{ref}} S_4(Q - Q^{-1})^2, \tag{24a}$$

$$\alpha_2 = \frac{1}{2}(\alpha_2^{\mathrm{ord}} + \alpha_3^{\mathrm{ord}})(1 + \lambda^{-1})S_2$$

$$= \frac{1}{2}\eta^{\mathrm{ref}}(Q^{-2} - Q^2)(1 + \lambda^{-1})S_2, \tag{24b}$$

$$\alpha_3 = \frac{1}{2}(\alpha_2^{\mathrm{ord}} + \alpha_3^{\mathrm{ord}})(1 - \lambda^{-1})S_2$$

$$= \frac{1}{2}\eta^{\mathrm{ref}}(Q^{-2} - Q^2)(1 - \lambda^{-1})S_2, \tag{24c}$$

$$\alpha_4 = \alpha_4^{\mathrm{ord}} + \frac{2}{15}\left(1 - \frac{10}{7}S_2 + \frac{3}{7}S_4\right)\alpha_1^{\mathrm{ord}}$$

$$+ \frac{1}{3}(1 - S_2)(\alpha_3^{\mathrm{ord}} - \alpha_2^{\mathrm{ord}})$$

$$= \eta^{\mathrm{ref}}\left[2 + \frac{(7 - 5S_2 - 2S_4)}{35}(Q - Q^{-1})^2\right], \tag{24d}$$

$$\alpha_5 = -S_2\alpha_2^{\mathrm{ord}} + \frac{2}{7}(S_2 - S_4)\alpha_1^{\mathrm{ord}}$$

$$= \eta^{\mathrm{ref}}(Q^2 - 1)S_2 - \frac{2\eta^{\mathrm{ref}}}{7}(Q - Q^{-1})^2(S_2 - S_4), \tag{24e}$$

$$\alpha_6 = -S_2\alpha_3^{\mathrm{ord}} + \frac{2}{7}(S_2 - S_4)\alpha_1^{\mathrm{ord}}$$

$$= \eta^{\mathrm{ref}}(Q^{-2} - 1)S_2 - \frac{2\eta^{\mathrm{ref}}}{7}(Q - Q^{-1})^2(S_2 - S_4). \tag{24f}$$

$$\gamma_1 = \frac{35 S_2^2 \gamma_1^{\text{ord}}}{14 + 5S_2 + 16S_4}$$

$$= \frac{35\eta^{\text{ref}}(Q^{-1} - Q)^2 S_2^2}{(14 + 5S_2 + 16S_4)}, \tag{24g}$$

$$\gamma_2 = \gamma_2^{\text{ord}} S_2 = \eta^{\text{ref}} S_2 (Q^{-2} - Q^2). \tag{24h}$$

$$\beta_1 = \frac{1}{2}(\alpha_2^{\text{ord}} + \alpha_3^{\text{ord}}) = \frac{1}{2}\eta^{\text{ref}}(Q^{-2} - Q^2). \tag{24h}$$

$$\lambda = \frac{(14 + 5S_2 + 16S_4)\lambda^{\text{ord}}}{35S_2}$$

$$= \frac{(14 + 5S_2 + 16S_4)}{35S_2} \frac{(Q^2 + 1)}{(Q^2 - 1)}. \tag{24j}$$

The additional viscosities due to compressibility effects remain identical to those given by [26] and are not repeated here.

Note that in the case of perfect alignment ($S_2 = S_4 = 1$), the viscosities (24) reduce to (13). Also the stress tensor (23) has the form recently proposed by Ericksen [33] for variable degree of alignment. When the order parameters are constant, then it corresponds exactly with the stress tensor (1) in the classical Ericksen-Lesile theory. This result clarifies the apparent discrepancy reported in [26].

It is seen from (24) that the viscosities have the following invariance:

$$\alpha_1(Q^{-1}) = \alpha_1(Q),$$

$$\alpha_2(Q^{-1}) = -\alpha_2(Q),$$

$$\alpha_3(Q^{-1}) = -\alpha_3(Q),$$

$$\alpha_4(Q^{-1}) = \alpha_4(Q),$$

$$\alpha_5(Q^{-1}) = \alpha_6(Q).$$

$$\gamma_1(Q^{-1}) = \gamma_1(Q),$$

$$\gamma_2(Q^{-1}) = -\gamma_2(Q).$$

$$\beta_1(Q^{-1}) = -\beta_1(Q),$$

$$\lambda(Q^{-1}) = \lambda(Q). \tag{25}$$

Thus using the above invariance we can express the viscosities of the discotic phase ($Q < 1$) in terms of the viscosities of the rod-like nematic phase ($Q > 1$).

B. Miesowicz Viscosities

Substitution of (24) in (5) yields

$$\frac{\eta_1}{\eta^{\text{ref}}} = \frac{S_2}{2}(Q^{-2} - 1) + \frac{(7 - 15S_2 + 8S_4)}{70}(Q - Q^{-1})^2 + 1$$

$$+ \frac{S_2}{4}\left(1 - \frac{35S_2(Q^2 - 1)}{(14 + 5S_2 + 16S_4)(Q^2 + 1)}\right)(Q^{-2} - Q^2),$$

$$\frac{\eta_2}{\eta^{\text{ref}}} = \frac{S_2}{2}(Q^2 - 1) + \frac{(7 - 15S_2 + 8S_4)}{70}(Q - Q^{-1})^2 + 1$$

$$- \frac{S_2}{4}\left(1 + \frac{35S_2(Q^2 - 1)}{(14 + 5S_2 + 16S_4)(Q^2 + 1)}\right)(Q^{-2} - Q^2),$$

$$\frac{\eta_3}{\eta^{\text{ref}}} = \frac{(7 - 5S_2 + 2S_4)}{70}(Q - Q^{-1})^2 + 1. \tag{26}$$

These expressions improve the corresponding ones given in [26]. For the Helfrich viscosity we obtain

$$\eta_{12} = -\eta^{\text{ref}} S_4 (Q - Q^{-1})^2, \tag{27}$$

which is identical to the result in [26]. The following invariance holds:

$$\eta_1(Q^{-1}) = \eta_2(Q),$$
$$\eta_3(Q^{-1}) = \eta_3(Q),$$
$$\eta_{12}(Q^{-1}) = \eta_{12}(Q). \tag{28}$$

In the case of random alignment ($S_2 = S_4 = 0$), the fluid is isotropic and we obtain for the viscosities

$$\eta_1 = \eta_2 = \eta_3 = \eta^{\mathrm{ref}}\left[1 + \frac{1}{10}(Q - Q^{-1})^2\right],$$
$$\eta_{12} = 0. \tag{29}$$

And in the case of perfect alignment ($S_2 = S_4 = 1$), they reduce to (14) as they should. Results for two different axis ratios are plotted in Figures 1 and 2 together with the results from a Fokker-Planck approach as outlined in the subsequent section. In view of the relations between $\eta_k(Q)$ and $\eta_j(Q^{-1})$ as given in (28), we plot only axis ratio $Q > 1$. For example, the Miesowicz viscosities for discotics with axis ratio $Q = 0.5$ can be deduced as follows: $\eta_1|_{Q=0.5} = \eta_2|_{Q=2}, \eta_2|_{Q=0.5} = \eta_1|_{Q=2}, \eta_3|_{Q=0.5} = \eta_3|_{Q=2}, \eta_{12}|_{Q=0.5} = \eta_{12}|_{Q=2}$.

V. COMPARISON WITH FOKKER-PLANCK CALCULATIONS

A. Summary

An alternative method for calculating the viscosities is based on a Fokker-Planck equation with a mean-field interaction. Here it will be shown to lead to a surprising similarity in qualitative results from the affine model. The following presentation is based on [12].

In mean field theory, we consider a single molecule having symmetry axis $\mathbf{u}(|\mathbf{u}| = 1)$ subject to a macroscopic flow $\nabla\mathbf{v} = \Gamma + \Omega$. The time evolution of the alignment u is determined by a balance of torques: hydrodynamic, brownian, external, and mean field. It is given by

$$\dot{u}_\mu = \Omega_{\mu\nu}u_\nu + B(\delta_{\mu\nu} - u_\mu u_\nu) - \Gamma_{\nu\kappa}u_\kappa$$
$$- D_r\partial_{u_\mu}(\log f + V/k_B T), \tag{30}$$

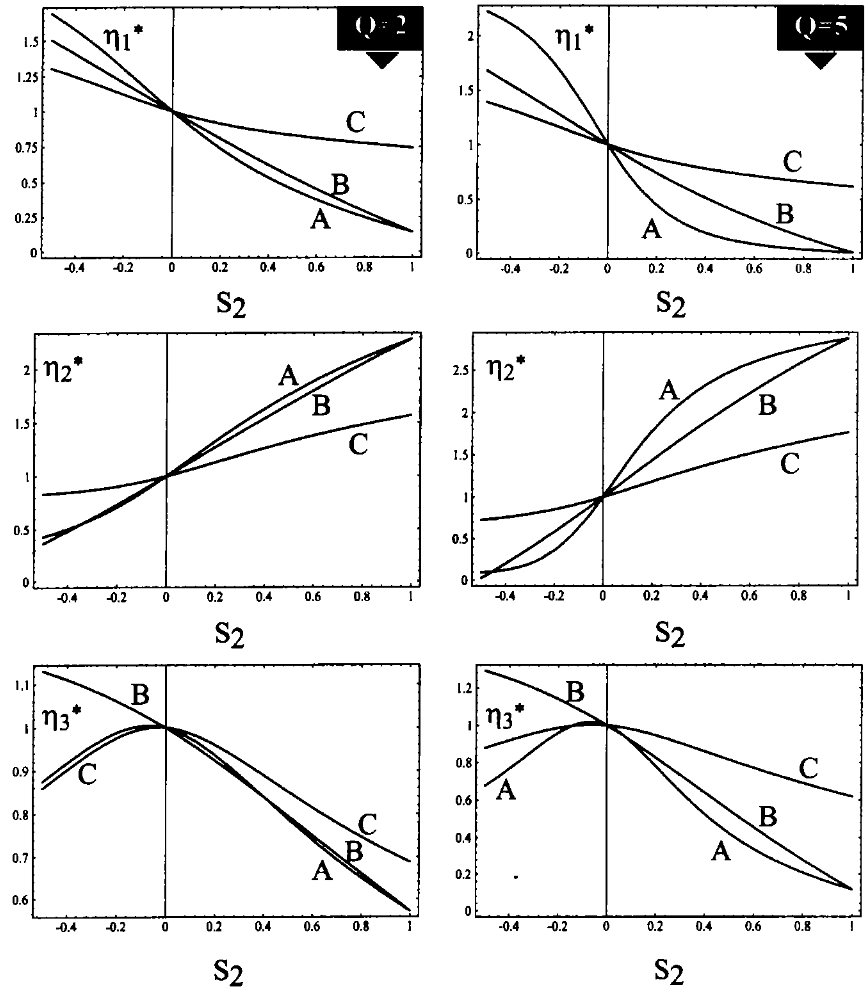

FIGURE 1 Dimensionless Miesowicz viscosities $\eta_k^* \equiv \eta_k/\bar{\eta}$ with $k = 1$, 2, 3 and $\bar{\eta} = (\eta_1 + \eta_2 + \eta_3)/3$ vs degree of alignment order parameter S_2. We report results for two different shapes of prolate molecules (axis ratio Q). Curve A corresponds to our results for the affine model, curve B to the original results of Ref. [27] and curve C to the Fokker-Planck approach.

where D_r is the effective rotary diffusion coefficient, $f(\mathbf{u})$ is the orientation distribution function, $V(\mathbf{u})$ is the potential, and B is a geometric factor usually taken as $(Q^2 - 1)/(Q^2 + 1)$. For this case, rod-like molecules correspond to $0 < B < 1$, disc-like molecules to $-1 < B < 0$. Commonly the potential $V(\mathbf{u})$ is taken as

$$V(\mathbf{u}) = V_{mf}(\mathbf{u}) + V_{\text{ext}}(\mathbf{u}), \tag{31}$$

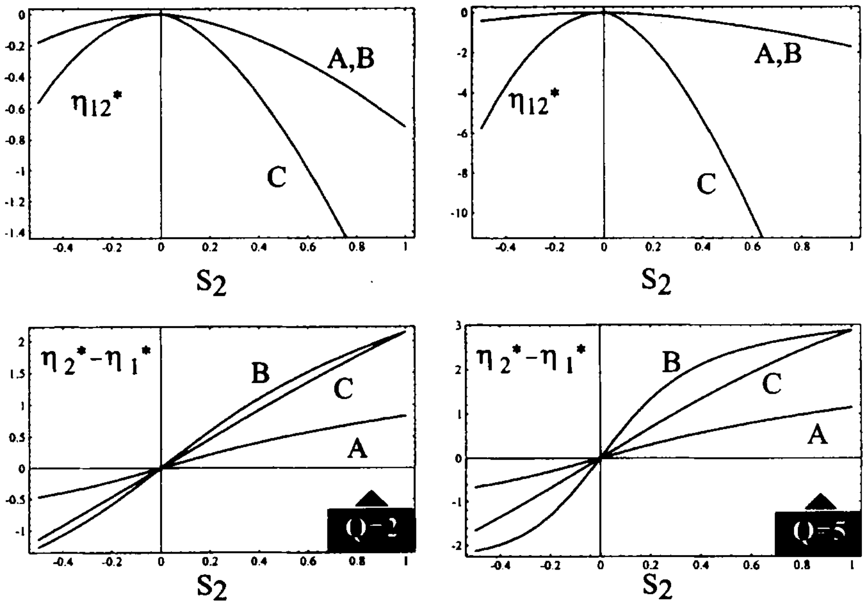

FIGURE 2 The first dimensionless Leslie viscosity coefficient $\eta_{12}^* \equiv \alpha_1^*$ and the difference between two Miesowicz viscosities η_1 and η_2 vs degree of alignment order parameter S_2 (labelling as in Fig. 1).

where

$$V_{\text{ext}}(\mathbf{u}) = -\frac{1}{2}\chi_a(\mathbf{H}\cdot\mathbf{u})^2,$$

$$V_{mf}(\mathbf{u}) = -\frac{3}{2}U_{mf}k_BT\langle u_\mu u_\nu\rangle u_\mu u_\nu. \tag{32}$$

V_{ext} denotes the contribution due to an induced dipole by an external field **H**, χ_a being the anisotropic susceptibility, and V_{mf} denotes the mean-field contribution, U_{mf} being a constant reflecting the energy intensity of the mean field.

The orientation distribution function $f(\mathbf{u})$ thus obeys the Fokker-Planck equation:

$$\frac{\partial f}{\partial t} = \partial_{u_\mu}[fD_r\partial_{u_\mu}(\log f + V/k_BT)]$$
$$-\partial_{u_\mu}[f\Omega_{\mu\nu}u_\nu + fB(\delta_{\mu\nu} - u_\mu y_\nu)\Gamma_{\nu\kappa}u_\kappa]. \tag{33}$$

$$\sigma_{\mu\nu}^{\mathrm{sym}} = 2\eta\Gamma_{\mu\nu} + \frac{1}{2}Bck_BT\,[\langle u_\mu\partial_{u_\nu}(\log f + V/k_BT)\rangle$$

$$+ \langle u_\nu\partial_{u_\mu}(\log f + V/k_BT)\rangle], \tag{34a}$$

$$\sigma_{\mu\nu}^{\mathrm{skw}} = -\frac{c}{2}[\langle u_\mu\partial_{u_\nu}V\rangle - \langle u_\nu\partial_{u_\mu}V\rangle]. \tag{34b}$$

With eq. (33) it can be rewritten as

$$\sigma_{\mu\nu}^{\mathrm{sym}} = 2\eta\Gamma_{\mu\nu} + \frac{Bck_BT}{2D_r}[B(\Gamma_{\mu\kappa}\langle u_\kappa u_\nu\rangle + \langle u_\mu u_\kappa\rangle\Gamma_{\kappa\nu} - 2\Gamma_{\kappa\lambda}\langle u_\kappa u_\lambda u_\mu u_\nu\rangle)$$

$$+ \Omega_{\mu\kappa}\langle u_\kappa u_\nu\rangle + \langle u_\mu u_\kappa\rangle\Omega_{\kappa\nu} - \partial_t\langle u_\mu u_\nu\rangle], \tag{35a}$$

$$\sigma_{\mu\nu}^{\mathrm{skw}} = -\frac{c}{2}[u_\mu\partial_{u_\nu}V_{\mathrm{ext}}\rangle - \langle u_\nu\partial_{u_\mu}V_{\mathrm{ext}}\rangle]. \tag{35b}$$

B. Viscosities

$$\alpha_1 = -\frac{B^2ck_BTS_4}{D_r}, \tag{36a}$$

$$\alpha_2 = -\frac{Bck_BT}{2D_r}(1 + \lambda^{-1})S_2, \tag{36b}$$

$$\alpha_3 = -\frac{Bck_BT}{2D_r}(1 - \lambda^{-1})S_2, \tag{36c}$$

$$\alpha_4 = 2\eta + \frac{B^2ck_BT}{35D_r}(7 - 5S_2 - 2S_4), \tag{36d}$$

$$\alpha_5 = \frac{Bck_BT}{2D_r}\left[\frac{B}{7}(3S_2 + 4S_4) + S_2\right], \tag{36e}$$

$$\alpha_6 = \frac{Bck_BT}{2D_r}\left[\frac{B}{7}(3S_2 + 4S_4) - S_2\right]. \tag{36f}$$

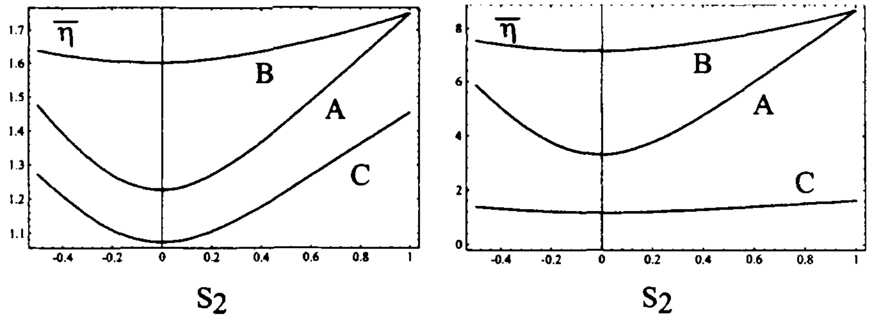

FIGURE 3 The viscosity $\bar{\eta}$ as defined in caption of Figure 1 vs degree of alignment order parameter S_2 (labelling as before).

$$\gamma_1 = \frac{Bck_BTS_2}{D_r\lambda}, \tag{36g}$$

$$\gamma_2 = -\frac{Bck_BTS_2}{D_r}. \tag{36h}$$

$$\beta_1 = -\frac{Bck_BT}{2D_r}. \tag{36i}$$

$$\lambda = \frac{(14 + 5S_2 + 16S_4)B}{35S_2}. \tag{36j}$$

Upon comparing these expressions with (24) from the affine model, we see that they have the same dependence on the alignment order parameters S_2 and S_4. Only in the dependence on the geometric factor do they differ. The corresponding Miesowicz viscosities as well as α_1 are plotted in Figures 1 and 2 from which the quantitative differences are obvious. In plotting the curves we use the closure relation $S_4 = S_2(1 - (1 - S_2)^{0.6})$ as motivated in [26].

VI. CONCLUSIONS

The Leslie and Miesowicz viscosities of partially aligned uniaxial liquid crystals have been calculated based on (i) the affine transformation model for perfectly aligned particles and (ii) assumption (17) relating the stress of a partially aligned fluid to that of a perfectly aligned fluid. The resulting macroscopic stress tensor has been shown to be of the form in the Ericksen-Leslie director theory when the degree of alignment is constant, resolving the apparent discrepancy found by [26]. This discrepancy seems to have been based on their assumption of hindered rotation used to simplify the calculations. Furthermore our results on the orientational dependence of the viscosities improve those of [26] by eliminating the simplifying approximations. The viscosities have also been shown to have the same orientational dependence as those obtained by a Fokker-Planck approach for the one partical distribution function. In fact, the affine model corresponds to the deterministic part of the equation of motion in the Fokker-Planck approach. In general, assumption (17) allows us to calculate the viscosities for models when we have the perfect alignment results. The same procedure for case of perfectly aligned biaxial particles [21] will lead to the viscosities for biaxial liquid crystals.

As already shown in Ref. [26], a proper choice of parameters can lead to a relatively good fit of the limited data available. More data over a large range of order parameters seems necessary in order to quantitatively evaluate the different models. Some work, for example, in this direction is presently being done by [34–36].

Acknowledgements

This work was financially supported by the "Sonderforschungsbereich 335: Anisotrope Fluide" of the DFG (Germany) and the Consiglio Nazionale delle Ricerche (Italy).

References

[1] G. Marrucci, *Mol. Cryst. Liq. Cryst.*, **72**, 153 (1982).
[2] A. N. Semonov, *Zh. Eksp. Teor. Fiz.*, **85**, 549 (1983).
[3] N. Kuzuu and M. Doi, *J. Phys. Soc. Jpn.*, **52**, 3486 (1983).
[4] M. A. Osipov and E. M. Terentjev, *Phys. Lett.*, A **134**, 301 (1989).
[5] M. A. Osipov and E. M. Terentjev, *Z. Naturforsch.*, **44a**, 785 (1989).
[6] M. A. Osipov and E. M. Terentjev, *Nuovo Cim.*, **12D**, 1223 (1990).
[7] E. M. Terentjev and M. A. Osipov, *Z. Naturforsch.*, **46a**, 733 (1991).
[8] V. I. Stepanov, *Z. Naturforsch.*, **47a**, 625 (1992).
[9] A. Chrzanowska and K. Sokalski, *Z. Naturforsch.*, **47a**, 565 (1992).
[10] P. Das and W. Schwarz, *Mol. Cryst. Liq. Cryst.* (1993).
[11] M. A. Osipov, T. J. Sluckin and E. M. Terentjev, *Liq. Crystals*, **19**, 197 (1995).
[12] M. Kröger and S. Sellers, *J. Chem. Phys.*, **103**, 807 (1995).
[13] L. A. Archer and R. G. Larson, *J. Chem. Phys.*, **103**, 3108 (1995).
[14] A. Chrzanowska and K. Sokalski, *Phys. Rev.*, E **52**, 5228 (1995).
[15] M. Fialkowski, *Phys. Rev. E*, **53**, 721 (1996).
[16] S. Hess, *Z. Naturforsch.*, **31a**, 1034 (1976).

[17] M. Doi, *J. Polym. Sci. Polym. Phys.*, **19**, 229 (1981).
[18] W. Helfrich, *J. Chem. Phys.*, **53**, 2267 (1970).
[19] D. Baalss and S. Hess, *Phys. Rev. Lett.*, **57**, 86 (1986).
[20] D. Baalss and S. Hess, *Z. Naturforsch.*, **43a**, 662 (1988).
[21] D. Baalss, *Z. Naturforsch.*, **45a**, 7 (1990).
[22] H. Sollich, D. Baalss and S. Hess, *Mol. Cryst. Liq. Cryst.*, **168**, 189 (1989).
[23] S. Hess, J. Schwarzl and D. Baalss, *J. Phys.: Condens. Matter*, **2**, SA279 (1990).
[24] S. Hess, D. Frenkel and M. Allen, *Molec. Phys.*, **74**, 765 (1991).
[25] S. Blenk, H. Ehrentraut, S. Hess and W. Muschik, *ZAMM*, **74**, 235 (1995).
[26] H. Ehrentraut and S. Hess, *Phys. Rev. E*, **51**, 2203 (1995).
[27] F. M. Leslie, *Quart. J. Mech. Appl. Math.*, **19**, 357 (1966).
[28] F. M. Leslie, *Arch. Ration. Mech. Anal.*, **28**, 265 (1968).
[29] F. M. Leslie, *Cont. Mech. Thermodyn.*, **4**, 167 (1992).
[30] S. Chandrasekhar, *Liquid Crystals, 2nd Ed.*, (Cambridge Univ. Press, 1992).
[31] W. Helfrich, *J. Chem. Phys.*, **51**, 4092 (1969).
[32] S. Hess and W. Köhler, *Formeln zur Tensorrechnung*, (Palm Enke, Erlangen, 1980).
[33] J. L. Ericksen, *Arch. Ration. Mech. Anal.*, **113**, 97 (1991).
[34] T. Kwok-Leung and S. D. Shine, Preprint: Estimation of the Miesowicz viscosity of liquid crystalline polymers from dynamic measurements.
[35] H. Gotzig, S. Grunenberghassanein and F. Noack, *Z. Naturforsch.*, **49a**, 1179 (1994).
[36] J. A. Muller, R. S. Stein and H. H. Winter, *Rheol. Acta*, **33**, 473 (1994).