Fokker-Planck calculations of the viscosities of biaxial fluids

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(Received 16 December 1996; revised manuscript received 15 April 1997)

A Fokker-Planck equation for the orientation distribution function is used to calculate the viscosity coefficients of the flow-induced biaxial phase. The results correspond to a special case of proposed phenomenological expressions for biaxial liquid crystals, but with a reduced number of coefficients, apparently due to assumptions on the symmetry of particles. In contrast to a previous calculation, our results satisfy the Onsager relations for the viscosities of biaxial fluids. Sample numerical values indicate that the contribution of flow-induced biaxiality can be significant in the shear viscosities, produce sign changes in the viscosity differences, and thus be important for the interpretation of shear flow data. [S1063-651X(97)05608-0]

PACS number(s): 61.30.Cz, 66.20.+d, 83.70.Jr

I. INTRODUCTION

The anisotropy of liquid crystals or suspensions leads to numerous viscosity coefficients in order to characterize the flow properties. Recently there has been some interest in calculating these viscosities from microscopic or mesoscopic models [1–10]. In general these molecular models (even with rodlike particles) indicate the presence of a biaxial phase or some degree of flow-induced biaxiality under shear. However, the viscosity calculations have been either restricted to the uniaxial phase or involved questionable mathematical simplifications.

Here we show how to extend the uniaxial calculations of [6,7] to the biaxial phase. We use a Fokker-Planck equation [11,12] for the one-particle orientation distribution function f to calculate the viscosities for the biaxial phase *without* approximating f, as commonly done. The model assumes rigid ellipsoidal particles with a mean-field interaction potential, thus we have

$$\partial_t f = \nabla_{u_i}[f D_r \nabla_{u_i}(\ln f + V/k_B T)] - \nabla_{u_i}[f\Omega_{ij}u_j + fB(\delta_{ij}-u_iu_j)A_{jk}u_k]. \qquad (1)$$

u is the symmetry axis of the ellipsoid, A and Ω are respectively the symmetric and skew symmetric parts of the macroscopic velocity gradient, $V=V_{\rm ext}+V_{\rm mf}$ is the potential of the external and mean fields, D_r is the rotary diffusion coefficient, and B is a particle geometric factor usually taken as $(r^2-1)/(r^2+1)$, r being the axis ratio. For this case, rodlike molecules correspond to $0<B<1$, disclike molecules to $-1<B<0$.

The viscous stress tensor σ for this model consists of a fluid plus a particle contribution and is given by (cf. [2])

$$\sigma^{\rm sym}_{\mu\nu} = 2\eta A_{\mu\nu} + \frac{Bck_BT}{2D_r}[B(A_{\mu\kappa}\langle u_\kappa u_\nu\rangle + \langle u_\mu u_\kappa\rangle A_{\kappa\nu} - 2A_{\kappa\lambda}\langle u_\kappa u_\lambda u_\mu u_\nu\rangle) + \Omega_{\mu\kappa}\langle u_\kappa u_\nu\rangle + \langle u_\mu u_\kappa\rangle\Omega_{\kappa\nu} - \partial_t\langle u_\mu u_\nu\rangle],$$

$$\sigma^{\rm skw}_{\mu\nu} = -\frac{c}{2}[\langle u_\mu \nabla_{u_\nu} V_{\rm ext}\rangle - \langle u_\nu \nabla_{u_\mu} V_{\rm ext}\rangle]. \qquad (2)$$

Section II shows how to obtain the moments of alignment. Relevant scalar order parameters are introduced and the viscosities are expressed in terms of them. For the biaxial phase we will obtain a stress tensor in terms of two directors and 11 distinct viscosities. In the uniaxial phase they reduce to the five independent viscosities recently calculated [6,7]. These results correspond to a special case of two phenomenological expressions for biaxial nematic liquid crystals proposed by (i) Chauré [13], which contained 12 independent viscosities, and by (ii) Leslie, Laverty, and Carlsson [14], which contained 16 viscosity coefficients related by four Onsager relations, all four Onsager relations being satisfied by our calculations.

Our results differ, however, from previous calculations on the number of viscosities [9] and on the validity of the Onsager relations [4]. Additionally our results satisfy only under certain conditions (i.e., highly aligned, rodlike particles) the proposed inequalities for rodlike biaxial nematics [15]. Finally, sample numerical values indicate that the effect of flow induced biaxiality can be significant, even producing sign changes in the shear viscosity differences. These results indicate that flow induced biaxiality could be important in interpreting data on shear flows.

II. MEASURES OF BIAXIAL ALIGNMENT

For uniaxial molecules with symmetry axis **u**, the symmetric, traceless (symbol "$\ulcorner\ \urcorner$") alignment tensor of rank two $\langle \overline{\mathbf{uu}} \rangle$ has three orthonormal eigenvectors **n,m,l** (i.e., directors). Since $\delta_{ij}=n_in_j+m_im_j+l_il_j$, we need only two directors (e.g., **n** and **m**). One thus obtains

$$\langle \overline{u_i u_j} \rangle = (S_2 + b/2)\overline{n_i n_j} + b\overline{m_i m_j}, \quad (3)$$

where the alignment order parameters S_2 and b are defined as averages of Legendre polynomials: $S_2 = \langle P_2(\mathbf{u}\cdot\mathbf{n})\rangle$, $b = \frac{2}{3}[\langle P_2(\mathbf{u}\cdot\mathbf{n})\rangle + 2\langle P_2(\mathbf{u}\cdot\mathbf{m})\rangle]$. They range in value by $-\frac{1}{2} \leqslant S_2 \leqslant 1$, $|b| \leqslant \frac{2}{3}(1 - S_2) \leqslant 1$. For perfect uniaxial alignment in the **n** direction, $S_2 = 1$ and $b = 0$. Thus b is called the biaxiality parameter. For perfect uniaxial alignment in the **m** direction, $b = -2S_2 = 1$. For random alignment (hence, isotropic) $S_2 = b = 0$.

Similarly, we obtain for the fourth-order alignment tensor

$$\langle \overline{u_\mu u_\nu u_\kappa u_\lambda} \rangle = (S_4 - \tfrac{3}{8}A_2 + \tfrac{1}{2}A_3)\overline{n_\mu n_\nu n_\kappa n_\lambda} + A_2 \overline{m_\mu m_\nu m_\kappa m_\lambda} + A_3 \overline{n_\mu n_\nu m_\kappa m_\lambda}, \quad (4)$$

where (using $\mathcal{P}_{\mathbf{x}} := \langle P_4(\mathbf{u}\cdot\mathbf{x})\rangle$, $\mathbf{x} = \mathbf{n},\mathbf{m},\boldsymbol{l}$) $S_4 = \mathcal{P}_{\mathbf{n}}$, $A_2 = \frac{8}{35}[4(\mathcal{P}_{\mathbf{m}} + \mathcal{P}_{\boldsymbol{l}}) - 3S_4]$, $A_3 = \frac{8}{35}[11\mathcal{P}_{\boldsymbol{l}} - 3(S_4 + \mathcal{P}_{\mathbf{m}})]$. Note that there are three distinct fourth-order scalar measures of alignment. In the uniaxial case $A_2 = A_3 = 0$, so that these two can be interpreted as fourth-order measures of the deviation from uniaxiality.

For convenience in notation we introduce two parameters as follows: $\widetilde{S}_2 := S_2 + b/2$, $\widetilde{S}_4 := S_4 - \frac{3}{8}A_2 + \frac{1}{2}A_3$. In general, all equations involving second and fourth moments for the biaxial case reduce to expressions for the unixial case by setting $b = A_2 = A_3 = 0$, $\widetilde{S}_2 = S_2$, and $\widetilde{S}_4 = S_4$.

III. RESULTS AND DISCUSSION

Inserting the expressions for the alignment tensors (3) and (4) into the stress tensor (2) and obtaining the two director equations from the second moment, we obtain in terms of the notation of [14] the following viscous stress tensor of an incompressible biaxial fluid [16]:

$$\begin{aligned}\sigma_{ij} = {} & \alpha_1 A_{kp} n_k n_p n_i n_j + \alpha_2 N_i n_j + \alpha_3 N_j n_i + \alpha_4 A_{ij} + \alpha_5 A_{ik} n_j n_k \\ & + \alpha_6 A_{jk} n_k n_i + \beta_1 A_{kp} m_k m_p m_i m_j + \beta_2 M_i m_j + \beta_3 M_j m_i \\ & + \beta_5 A_{ik} m_j m_k + \beta_6 A_{jk} m_k m_i + N_p m_p(\mu_1 m_i n_j + \mu_2 n_i m_j) \\ & + \mu_5 m_k m_p A_{kp} n_i n_j + A_{kp} n_k m_p(\mu_3 m_i n_j + \mu_4 n_i m_j), \end{aligned} \quad (5)$$

where the corotational director times derivatives **N** and **M** are defined as $N_i := \dot{n}_i - \Omega_{ik} n_k$, $M_i := \dot{m}_i - \Omega_{ik} m_k$, and the viscosities are given explicitly by (with $\chi := ck_B T/2D_r$):

$$\alpha_1 = -2\chi B^2 \widetilde{S}_4, \quad \alpha_5 = \chi B\left[\frac{B}{7}(3\widetilde{S}_2 + 4\widetilde{S}_4 + 3A_3) + \widetilde{S}_2\right],$$

$$\alpha_2 = -\chi B(1 + G_1)\widetilde{S}_2, \quad \alpha_3 = -\chi B(1 - G_1)\widetilde{S}_2,$$

$$\alpha_4 = 2\eta + \chi\frac{B^2}{35}(14 - 10\widetilde{S}_2 - 4\widetilde{S}_4 - 10b - 4A_2 - 13A_3),$$

$$\alpha_6 = \alpha_5 - 2\chi B\widetilde{S}_2, \quad \beta_6 = \beta_5 - 2\chi Bb, \quad \beta_1 = -2\chi B^2 A_2,$$

$$\beta_2 = -\chi B(1 + G_2)b, \quad \beta_3 = -\chi B(1 - G_2)b,$$

$$\beta_5 = \chi B\left[\frac{B}{7}(3b + 4A_2 + 3A_3) + b\right], \quad \mu_5 = 0$$

$$\mu_1 = -\mu_2 = \chi B G_1(1 + G_3)b, \quad \mu_3 = \mu_4 = \chi B^2 A_3. \quad (6)$$

For simplicity we have collected order parameters in the following three groups:

$$G_1 := \frac{35\widetilde{S}_2}{B(14 + 5\widetilde{S}_2 + 16\widetilde{S}_4 - 10b - 4A_2 + 2A_3)},$$

$$G_2 := \frac{35b}{B(14 + 5b + 16A_2 - 10\widetilde{S}_2 - 4\widetilde{S}_4 + 2A_3)},$$

$$G_3 := \frac{B\widetilde{S}_2(3b + 4A_2 - 4A_3)}{b(3\widetilde{S}_2 + 4\widetilde{S}_4 - 4A_3)}. \quad (7)$$

The viscosity coefficients γ_i, λ_i associated with the two director equations are determined from Eq. (6) through [14] $\gamma_1 = \alpha_3 - \alpha_2$, $\gamma_2 = \alpha_6 - \alpha_5$, $\gamma_3 = \mu_2 - \mu_1$, $\lambda_1 = \beta_3 - \beta_2$, $\lambda_2 = \beta_6 - \beta_5$, $\gamma_4 = \mu_4 - \mu_3$. As they should, the viscosities have the following invariance: α_i and β_i are exchanged when $\widetilde{S}_2$ with b and $\widetilde{S}_4$ with A_2 are exchanged.

It is easily verified from Eq. (6) that the calculated viscosities satisfy the following proposed Onsager relations [14]:

TABLE I. Numerical values of the dimensionless viscosity coefficients for *rods (B=1)* $\eta^*_{a,b} = (\eta_{a,b} - \eta)/\chi$ with $\mathbf{a},\mathbf{b} \in$ {''$-$'' (=shear direction), ''$|$'' (=velocity gradient), ''$\circ$'' (=vorticity), ''$/,\backslash$'' (=in shearing plane at 45°, 135° with respect to shear direction)}. A viscosity $\eta_{a,b}$ is measured when $\mathbf{n}\|\mathbf{a}$, $\mathbf{m}\|\mathbf{b}$. The last three rows contain all rotational viscosities as defined in the text. For the given values of order parameters (the left part of the table) the viscosity coefficients are obtained by evaluating the Leslie coefficients from Eqs. (7) and (8). In the text, the analytical expressions for the viscosities are given for the general case of ellipsoids of revolution with an arbitrary shape (e.g., disks, spheres), where $|B| \leqslant 1$.

S_2	S_4	b	A_2	A_3	$\eta^*_{-\circ}$	$\eta^*_{-\vert}$	$\eta^*_{\circ -}$	$\eta^*_{\circ \vert}$	$\eta^*_{\vert -}$	$\eta^*_{\vert \circ}$	$\eta^*_{-/}$	$\eta^*_{\backslash \circ}$	$\eta^*_{/\backslash}$	γ_n	γ_m	γ_{nm}
1.0	1.0	0.0	0.0	0.0	0.000	0.000	0.000	0.000	2.000	2.000	0.500	0.000	0.500	2.000	0.000	2.000
0.7	0.5	0.0	0.0	0.0	0.001	0.001	0.071	0.071	1.401	1.401	0.451	0.071	0.451	1.345	0.000	1.345
0.7	0.5	0.1	0.0	0.0	0.001	0.015	0.006	0.206	1.458	1.501	0.486	0.106	0.501	1.591	0.140	1.731
0.7	0.5	0.2	0.1	0.0	0.016	0.048	0.000	0.400	1.591	1.616	0.538	0.150	0.584	1.948	0.415	2.363
0.7	0.4	0.2	0.1	0.1	0.020	0.025	0.000	0.400	1.611	1.620	0.562	0.150	0.614	2.000	0.392	2.392

$$\alpha_2+\alpha_3=\alpha_6-\alpha_5, \quad \beta_2+\beta_3=\beta_6-\beta_5,$$

$$\mu_1+\mu_2=\mu_4-\mu_3, \quad \mu_5=0. \tag{8}$$

In this case the expressions proposed for the viscous stress tensor in [13] and [14] become equivalent, containing 12 independent coefficients. We obtain from our calculations, however, the additional relation

$$\mu_1+\mu_2=0, \quad \text{hence} \;\; \mu_3=\mu_4. \tag{9}$$

That is, there are at most 11 distinct viscosities for the stress tensor in terms of the eight parameters η, χ, B, S_2, b, S_4, A_2, and A_3. As discussed in [14] the μ_i are viscosities that represent coupling between the directors **n** and **m**. Thus the molecular model indicates a simplified form of coupling, apparently due to the symmetric ellipsoidal shape of the particles. More complex shaped particles could have particle-particle interactions that lead to more viscosities. Thus deviations from Eq. (9) could be used as a measure for the particle biaxiality.

Additional viscosities that represent the effective shear and rotational viscosities (see table caption) have been introduced and expressed through the α_i, β_i, μ_i [15] via

$$\begin{pmatrix} 2\eta^*_{-\circ} \\ 2\eta^*_{-|} \\ 2\eta^*_{\circ -} \\ 2\eta^*_{\circ |} \\ 2\eta^*_{|-} \\ 2\eta^*_{|\circ} \\ 4\eta^*_{-/} \\ 4\eta^*_{\backslash\circ} \\ 4\eta^*_{/\backslash} \\ \gamma_n \\ \gamma_m \\ \gamma_{nm} \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 & 0 & 1 & 0 & -1 & 0 & -1 & 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & -1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 1 & 1 & 0 & 0 & 0 & 1 & 0 & 1 & -1 & 0 & 1 & 0 \\ 0 & -1 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & -2 & 2 & 4 & 2 & 2 & 1 & -2 & 2 & -2 & 2 & -2 & 2 & 1 & 1 \\ 0 & 0 & 0 & 4 & 0 & 0 & 1 & -2 & 2 & 2 & 2 & 0 & 0 & 0 & 0 \\ 1 & -2 & 2 & 4 & 2 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 1 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & -1 & 1 & 0 & 0 \end{pmatrix}$$

$$\times(\alpha_1,\alpha_2,\alpha_3,\alpha_4,\alpha_5,\alpha_6,\beta_1,\beta_2,\beta_3,\beta_5,\beta_6,\mu_1,\mu_2,\mu_3,\mu_4)^{\dagger}.$$

Table I illustrates sample numerical values of these dimensionless viscosity coefficients for ideal rods ($B=1$). It demonstrates that small, but nonzero biaxiality ($b\neq 0$) can produce substantial changes. Relationships between all of the five order parameters have not yet been established, either experimentally nor theoretically, so that we do not introduce any decoupling assumption into the model here. The table already provides the necessary information about the order of the viscosities when corrections due to a biaxial distortion have to be taken into account. The results predict, as visible from the table, e.g., a sign change for the difference $\eta^*_{-|}-\eta^*_{\circ -}$ with increasing biaxiality. More detailed calculations are being presently investigated.

Carlsson, Leslie, and Laverty [15] proposed, for rodlike biaxial nematics, several inequalities among the viscosities. Rodlike corresponds to setting $B>0$ in our model. It is easy to verify from Eq. (6) that the inequalities are satisfied for $B\approx 1$. However, our result limits the validity to certain ranges for the order parameters and the shape coefficient.

For the uniaxial phase with director **n** (i.e., $b=A_2=A_3=0$), the β_i and μ_i vanish and the results reduce to those given previously in [6,7]. Alternatively, for the case of uniaxial alignment in the **m** direction (i.e., $\widetilde{S}_2=\widetilde{S}_4=A_3=0$), the α_i and μ_i vanish, and the coefficients β_i and G_2^0 become identical to the corresponding uniaxial coefficients.

Our present calculations provide an extension of these results for flow-induced biaxiality. They can provide the basis for discussing the qualitative flow behavior and the interpretation of experimental data as has already been done in the uniaxial case. In the special case of uniaxial phase the result (6) and the qualitative flow behavior, which is usually expressed in terms of G_1^0 [see Eq. (7)], have been already compared successfully with experimental findings [7,17].

ACKNOWLEDGMENTS

This work was financially supported by the Minerva Foundation, Munich (Germany) and the Consiglio Nazionale delle Ricerche (Italy).

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