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Anisotropy of the viscosity of nematic liquid crystals and of oriented ferro-fluids via non-equilibrium molecular dynamics

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Abstract. The anisotropy of the viscosity and the flow alignment of nematic and nematic discotic liquid crystals as well as that of oriented ferro-fluids are described by the same set of viscosity coefficients. Results obtained from NEMD computer simulations are reported for completely aligned nematics and for perfectly oriented ferro-fluids.

1. Introduction

The combination of 'fluidity' (the typical property of a 'liquid') and 'anisotropy' (usually associated with 'crystalline' materials) provides one of the fascinations of liquid crystals and of other anisotropic fluids. In this article, results for the 'anisotropy of the viscosity' and the flow alignment coefficients as obtained from non-equilibrium molecular dynamics (NEMD) computer simulations are presented for nematic and nematic discotic crystals as well as for oriented ferro-fluids. A comparison with theoretical model calculations and experimental data is made. Firstly, some remarks on the viscosity coefficients are in order.

2. Viscosity coefficients

The (local) orientation of a nematic liquid crystal is specified by a unit vector \mathbf{n} , termed the 'director'. If a viscous flow takes place in the presence of a (strong) orienting electric or magnetic field which determines the direction of \mathbf{n} , the effective viscosity depends on the relative orientation of \mathbf{n} with respect to the flow geometry. Four orientations suffice to describe the anisotropy of the shear viscosity [1]. For the meaning of the three Miesowicz coefficients η_1 , η_2 , η_3 and of η_4 , see figure 1. Let $p_{yx}^{(i)}$ be the yx component of

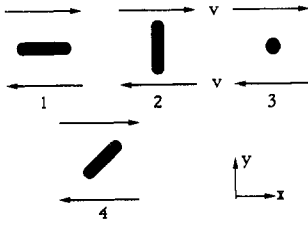


Figure 1. The principal directions 1–4 of the field-induced orientation of the molecules with respect to the flow velocity v and its gradient.

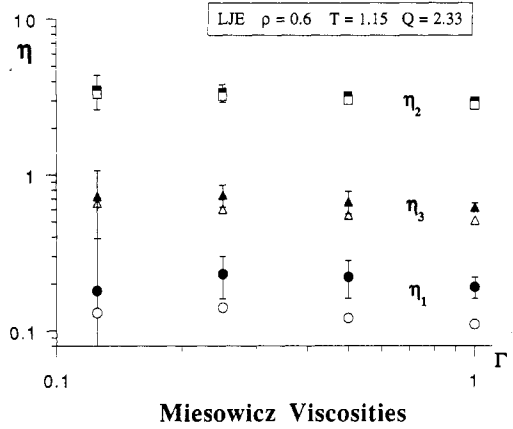


Figure 2. The Miesowicz viscosities η_1, η_2, η_3 as function of the shear rate Γ in a double-logarithmic plot for the LJ fluid with the axis ratio $Q = \frac{2}{3}$ at the density $\rho = 0.6$ and the temperature $T = 1.15$: \circ, \bullet , direction 1; \square, \blacksquare , direction 2; $\triangle, \blacktriangle$, direction 3; $\circ, \triangle, \square$, the potential contribution; $\bullet, \blacktriangle, \blacksquare$, the total (sum of the potential and the kinetic contributions) viscosity coefficients.

the pressure tensor for these orientations ($i = 1, 2, 3, 4$) and $\Gamma = \partial v_x / \partial y$, the shear rate of a plane Couette flow. Then the coefficients η_i are defined by

$$p_{yx}^{(i)} = -\eta_i \Gamma. \quad (1)$$

Instead of η_4 , the ‘Helfrich coefficient’

$$\eta_{12} = 4\eta_4 - 2(\eta_1 + \eta_2) \quad (2)$$

is used. The Leslie coefficients γ_1 and γ_2 occur in connection with the torque acting on the molecules or the antisymmetric part of the pressure tensor [1–3]:

$$2(p_{yx}^{(1)} - p_{xy}^{(1)}) = \gamma_1 + \gamma_2 \quad 2(p_{yx}^{(2)} - p_{xy}^{(2)}) = \gamma_1 - \gamma_2 \quad (3)$$

where the superscripts 1 and 2 refer to the orientations of \mathbf{n} specified above. The coefficient γ_2 is linked with η_1 and η_2 by the Onsager–Parodi relation

$$\gamma_2 = \eta_1 - \eta_2. \quad (4)$$

An additional coefficient, denoted by κ , has to be considered even for a divergence-free flow of a nematic liquid crystal. It is defined by [2, 3]

$$2\delta p^{(4)} = -\kappa \Gamma \quad (5)$$

where $\delta p = p - p_{eq}$ is the change in the scalar pressure (one third of the trace of the pressure tensor) and the superscript (4) refers to the specific orientation. The coefficients γ_2, η_{12} and κ may have either sign.

Ordinary nematic liquid crystals are composed of rod-like (prolate) molecules. Fluids of disc-like (oblate) molecules may also possess a nematic phase which is referred to as nematic discotic. Ferro-fluids are dispersions containing (spherical) colloidal particles

with a core composed of magnetized iron or cobalt. The magnetic moments of these particles can be aligned by a magnetic field. Apart from the Hall-effect-like contributions to the transport coefficients which are odd in the applied magnetic field, an oriented ferro-fluid is characterized by the same set of viscosity coefficients as a nematic liquid crystal [2].

3. Non-equilibrium molecular dynamics

Model fluids composed of perfectly oriented non-spherical particles are studied by NEMD techniques where a plane Couette flow is simulated in analogy to previous investigations on simple fluids [4–8].

3.1. Model potentials

The potentials used to model perfectly aligned *nematic* and *nematic discotic fluids* are related to spherical interaction potentials by an affine transformation. The anisotropic binary interaction potential $\Phi_A(\mathbf{r})$ is given by

$$\Phi_A(\mathbf{r}) = \Phi_{\text{sph}}(\mathbf{r}^A) \quad (6)$$

where Φ_{sph} is the spherical interaction potential and

$$\mathbf{r}^A \cdot \mathbf{r}^A = \mathbf{r} \cdot \mathbf{A} \cdot \mathbf{r} \quad (7)$$

with a positive definite (transformation) matrix \mathbf{A} . It describes the mapping of the sphere $\mathbf{r}^A \cdot \mathbf{r}^A = \text{constant}$ on an ellipsoid. If the eigenvalues A_i , $i = 1, 2, 3$ obey the relation $A_1 A_2 A_3 = 1$, the volume is conserved. For uniaxial particles with their symmetry axis parallel to the unit vector \mathbf{u} and the axis ratio $Q = a/b$ of the semiaxes a and $b = c$ of the equipotential surfaces, one has

$$\mathbf{r}^A \cdot \mathbf{r}^A = Q^{2/3} [\mathbf{r} \cdot \mathbf{r} + (Q^{-2} - 1)(\mathbf{r} \cdot \mathbf{u})^2]. \quad (8)$$

Owing to the complete orientation (Maier–Saupe order parameter $S = 1$), \mathbf{u} is equal to the director \mathbf{n} . Specific choices of \mathbf{u} with respect to the flow direction and its gradient are made in accord with the preferential directions 1–4. Nematics and nematic discotic fluids are distinguished by $Q > 1$ (prolate) and $Q < 1$ (oblate). For Φ_{sph} the soft sphere (ss) r^{-12} and the Lennard-Jones (LJ) $4(r^{-12} - r^{-6})$ potential were used; the corresponding ellipsoidal particles are referred to as ‘soft ellipsoids’ (SE) and Lennard-Jones ellipsoids (LJE).

The *ferro-fluid* is modelled by a ss potential with embedded dipoles with the magnetic moment $\boldsymbol{\mu} = \mu \mathbf{n}$ where μ is the magnitude of the moment and \mathbf{n} is the unit vector parallel to the external magnetic field which determines the direction of $\boldsymbol{\mu}$. The resulting potential is ($\hat{\mathbf{r}} = r^{-1} \mathbf{r}$)

$$\Phi = r^{-12} - 3\mu^2 r^{-3} [(\mathbf{n} \cdot \hat{\mathbf{r}})^2 - \frac{1}{3}]. \quad (9)$$

Again, \mathbf{n} is chosen to be parallel to the special directions mentioned above. Physical variables are expressed in standard ss [4–7] and LJ [4–7] units. The potential are cut off at $r_c = 2.5$.

3.2. Pressure tensor and viscosities

In the NEMD simulation, the components of the pressure tensor \mathbf{p} are evaluated according to

Table 1. The viscosity coefficients $\eta_1, \eta_2, \eta_3, \eta_{12}, \gamma_1, \gamma_2$ and κ for the LJE and SE model fluids with $Q = \frac{7}{3}$ and $Q = \frac{3}{2}$ (at $\rho = 0.6, T = 1.15$ and $\rho = 0.6, T = 0.25$, respectively) as well as for the SSD model ferro fluid with $\mu^2 = 0.8$ (at $\rho = 0.6, T = 0.25$).

| | LJE $Q = \frac{7}{3}$ | LJE $Q = \frac{3}{2}$ | SE $Q = \frac{7}{3}$ | SE $Q = \frac{3}{2}$ | SSD $\mu^2 = 0.8$ |
|-------------|--------------------------|--------------------------|-------------------------|-------------------------|----------------------|
| η_1 | 0.15 ± 0.04 | 3.1 ± 0.1 | 0.09 ± 0.03 | 2.7 ± 0.3 | 0.63 ± 0.05 |
| η_2 | 3.5 ± 0.3 | 0.17 ± 0.06 | 2.8 ± 0.3 | 0.10 ± 0.02 | 0.43 ± 0.04 |
| η_3 | 0.70 ± 0.10 | 0.80 ± 0.1 | 0.52 ± 0.10 | 0.55 ± 0.1 | 0.50 ± 0.04 |
| η_{12} | -2.1 ± 0.4 | — | -1.8 ± 0.3 | — | 2.0 ± 0.1 |
| γ_1 | 2.2 ± 0.4 | 2.0 ± 0.1 | 1.9 ± 0.3 | 1.9 ± 0.3 | 0.16 ± 0.02 |
| γ_2 | -3.5 ± 0.4 | 2.9 ± 0.1 | -2.7 ± 0.3 | 2.7 ± 0.3 | 0.17 ± 0.02 |
| κ | 0.0 ± 0.04 | — | 0.0 ± 0.03 | — | 0.6 ± 0.02 |

$$V\mathbf{p} = \left\langle \sum_i \mathbf{c}^i \mathbf{c}^i \right\rangle + \frac{1}{2} \left\langle \sum_{i \neq j} \mathbf{r}^{ij} \mathbf{F}^{ij} \right\rangle. \quad (10)$$

Here V is the volume of the periodicity box containing N particles; \mathbf{c}^i is the particular velocity of particle i , $\mathbf{r}^{ij} = \mathbf{r}^i - \mathbf{r}^j$ is the difference between the position vectors of particles i and j ; \mathbf{F}^{ij} is the force acting between them. The angular brackets $\langle \dots \rangle$ refer to an average over many (typically 10^4 – 10^5) time steps. The two terms on the RHS of equation (10) are referred to as the ‘kinetic’ and the ‘potential’ contributions to the pressure tensor.

The plane Couette flow is generated by the homogeneous shear algorithms [4, 9]. At a prescribed shear rate $\Gamma = \partial v_x / \partial y$, the viscosities of interest can be inferred from the yx and xy components of the pressure tensor (for the various orientations of the non-spherical particles) according to (1)–(3); furthermore κ is obtained from the shear-induced change of the trace of the pressure tensor (cf (5)). In figure 2, the Miesowicz viscosities η_1, η_2, η_3 are displayed as functions of Γ for an LJE fluid with the axis ratio $Q = \frac{7}{3}$ at the (reduced) density and temperature $\rho = 0.6$ and $T = 1.15$ (LJ units; $N = 128$). A shear rate dependence of the viscosity (non-Newtonian behaviour) has also been observed in NEMD simulations of simple fluids [4–7]. The viscosity coefficients reported here are their ‘Newtonian values’ obtained for small Γ .

In table 1, NEMD results are listed for the LJE fluids ($\rho = 0.6, T = 1.15$; reduced LJ units; $N = 128$) with $Q = \frac{7}{3}$ (nematic) and $Q = \frac{3}{2}$ (nematic discotic); for the SE fluids ($\rho = 0.6, T = 0.25$; reduced ss units) also with $Q = \frac{7}{3}$ and $Q = \frac{3}{2}$ and for the model ferro-fluid referred to as ‘soft spheres with dipoles’ (SSDs) at the state point $\rho = 0.6, T = 0.25$ (reduced ss units; $N = 512$) with the magnitude μ of the dipole moment given by $\mu^2 = 0.8$. For the cases $Q = \frac{3}{2}$ no simulations for the geometry 4 were performed; therefore the data for η_{12} and κ are not available. The state points for ellipsoidal fluids were chosen such that one is not in the vicinity of a transition to a positionally ordered state [2, 3, 8]. In the model ferro-fluid this cannot be excluded. A number of remarks are in order.

(i) In nematics ($Q > 1$), the expected sequence

$$\eta_2 > \eta_3 > \eta_1 \quad \gamma_2 < 0 \quad (11)$$

is found for the Miesowicz viscosities. For nematic discotics ($Q < 1$), one has

$$\eta_1 > \eta_3 > \eta_2 \quad \gamma_2 > 0. \quad (12)$$

(ii) The model ferro-fluid obeys the inequalities (12) of a discotic substance. This seems surprising at first glance since the magnetic particles have a tendency to form chain-like structures [10, 11]. On the other hand, the ‘shape’ of the oriented dipolar particles determined by the equipotential surface where Φ equals the temperature T is oblate (corresponding to $Q < 1$). For $\mu^2 = 0.8$, the effective axis ratio is $Q \approx 0.63$.

(iii) The Onsager–Parodi relation (4) is obeyed within the computational accuracy.

(iv) In all cases studied, the inequality $|\gamma_2| > \gamma_1$ applies, which is necessary for a stable flow alignment in nematic liquid crystals.

(v) The negative sign of η_{12} and $\kappa \approx 0$ for the ellipsoidal fluids is in accord with theoretical calculations [2, 8] (cf section 4). For oblate ellipsoids one also expects $\eta_{12} < 0$ and $\kappa \approx 0$. With regards to these coefficients, the model ferro-fluid behaves differently.

Furthermore, the potential contribution to the pressure tensor of the SSD fluid (in contradistinction to the SE and LJE fluids) is anisotropic in thermal equilibrium. This implies that $p_{xy} \neq 0$ in geometry 4 even for $\Gamma = 0$. A positive sign of κ means a partial destruction of that anisotropy by the shear flow.

4. Comparison with theory and experiments

4.1. Nematic liquid crystals

For the affine transformation model originally proposed by Helfrich [12], the potential contributions η_i^{pot} to the viscosity coefficients η_i can be expressed in terms of the axis ratio Q and the viscosity of a reference fluid composed of spherical particles [2, 8]. The theoretical results needed here are

$$\eta_3^{\text{pot}}/\eta_1^{\text{pot}} = \eta_2^{\text{pot}}/\eta_3^{\text{pot}} = Q^2 \quad (13)$$

$$\gamma_1/\eta_3^{\text{pot}} = (Q - Q^{-1})^2 \quad (14)$$

$$\eta_{12} = -\gamma_1 \quad \kappa = 0. \quad (15)$$

The data listed in table 1 for the LJE and SE fluids obey relation (15). The total viscosity coefficients η_i given in table 1 are the sum of η_i^{kin} and η_i^{pot} ; the kinetic contributions η_i^{kin} are small, but not negligible. The NEMD data for the ratios η_3/η_1 , η_2/η_3 , γ_1/η_3 and $-\eta_{12}/\gamma_1$ agree well with the theoretical predictions. The agreement with experimental data [13] is fair although the ratios η_3/η_1 and $-\eta_{12}/\gamma_1$ are overestimated by both the theory and the simulations based on the affine transformation model.

4.2. Ferro-fluids

The simulations show that all viscosity coefficients required for nematics are also non-zero for ferro-fluids. Early theoretical considerations [14] attributed the anisotropy of the flow properties of ferro-fluids solely to $\gamma_1 \neq 0$ and $\eta_3 \neq \frac{1}{2}(\eta_1 + \eta_2)$ but ignored the possibilities of having $\eta_1 \neq \eta_2$, $\gamma_2 \neq 0$ and $\eta_{12} \neq 0$. Application of an affine transformation model with an effective $Q \approx 0.63$ overestimates the anisotropy of the Mie-sowicz viscosities and cannot account for $\eta_{12} > 0$ and $\kappa > 0$.

Measurements of a Poiseuille flow through a pipe with circular cross-section yielded [15]

$$\eta^{\parallel} - \eta^{\perp} = \eta_1 - \frac{1}{2}(\eta_2 + \eta_3) > 0 \quad (16)$$

where \parallel and \perp refer to the magnetic field parallel and perpendicular to the flow direction. The NEMD data for the SSD fluid listed in table 1 also obey the inequality (16). The need to use the full set of the nematic viscosity coefficients for ferro-fluids was also noticed on account of theoretical considerations and of experimental data [16].

4.3. Concluding remarks

For nematics close to the transition to a smectic phase, the smallest viscosity η_2 (n parallel to the flow direction) increases strongly; the order (10) is no longer obeyed and η_{12} is positive [13]. A similar behaviour is expected for nematic discotic substances close to a transition into a columnar phase. The ellipsoidal SE and LJE model treated here do not possess a smectic phase [17]; the model ferro-fluid, however, can undergo a transition to columnar and lamellar phase [11, 18]. This fact might explain $\eta_{12} > 0$.

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