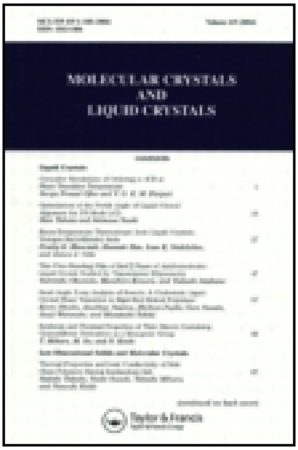

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Anisotropy of the Viscosity of a Nematic Discotic Liquid Crystal via Non-Equilibrium Molecular Dynamics

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Viscosity coefficients analogous to the Miesowicz viscosities η_1, η_2, η_3 and to the Leslie coefficients γ_1 and γ_2 are determined for an oriented nematic discotic liquid crystal in molecular dynamics computer simulations and compared with theoretical calculations.

Keywords: viscosity, flow alignment, nematic discotics, non-equilibrium molecular dynamics

Theoretical considerations based on an affine transformation model[1] suggest close similarities but also some qualitative differences between the anisotropy of the viscosity of ordinary nematics (N) and of nematic discotic (N_D) liquid crystals.[2] A test of the theoretical predictions via a nonequilibrium molecular dynamics [NEMD] computer simulation is presented in this note. More specifically, viscosity coefficients analogous to the Miesowicz viscosities η_1, η_2, η_3 and the Leslie coefficients γ_1 and γ_2 of nematics[3] are determined for discotics modelled by an anisotropic fluid composed of oriented oblate particles (disks). This extends our previous studies on fluids of oriented prolate particles.[1] The present investigations may give some hints and, hopefully, motivations for experimental studies on the flow properties and flow alignment of N_D liquid crystals. A good candidate is the recently synthesized super-disk-like hexaphenylethynylbenzene[4] which exhibits a rather broad N_D phase with a relatively low viscosity (compared with other discotics).

THEORETICAL CONSIDERATIONS

The viscosity of a fluid, in general, is the sum of a "kinetic" and of a "potential" contribution.[5] The dominating potential contribution to the Miesowicz viscosities η_i^{pot} (i = 1, 2, 3) and the Leslie coefficients γ_1, γ_2 of a model liquid of perfectly oriented ellipsoidal particles[6] can be expressed in terms of a single viscosity coefficient η^{pot} and the ratio Q between the figure axis and one of the two other axes of a particle. The quantity η^{pot} is the potential contribution to the viscosity of a reference fluid of spherical particles related to the anisotropic fluid by a volume conserving affine transformation of the equipotential surfaces describing the molecular interaction. The results of the theory are[1]

$$\eta_1^{pot} = Q^{-2}\,\eta^{pot}, \quad \eta_2^{pot} = Q^2\,\eta^{pot}, \; \eta_3^{pot} = \eta^{pot}, \tag{1}$$

$$\gamma_1 = (Q - Q^{-1})^2\,\eta^{pot}, \; \gamma_2 = (Q^{-2} - Q^2)\,\eta^{pot}. \tag{2}$$

There is no kinetic contribution to the Leslie coefficients γ_1 and γ_2. For this reason the superscript "pot" is not needed. The labels 1, 2, 3 of the Miesowicz viscosities η_i correspond to the director (symmetry axis of the particles) oriented parallel to the x, y, z coordinate axes where the flow is in x-direction, and the fluid is confined by flat planes perpendicular to the y-direction. Thus for the components of the flow velocity v one has

$$v_x = v(y), \quad v_y = 0, \; v_z = 0.$$

The expressions (1) and (2) apply both to fluids of prolate ($Q > 1$) and of oblate ($Q < 1$) particles. Notice that $\eta_1^{pot} = \eta_2^{pot} = \eta_3^{pot}$ and $\gamma_1 = \gamma_2 = 0$ for spherical particles ($Q = 1$). For ordinary nematics ($Q > 1$), one has

$$\eta_1^{pot} < \eta_3^{pot} < \eta_2^{pot} \text{ and } \gamma_2 < 0, \tag{3}$$

whereas

$$\eta_1^{pot} > \eta_3^{pot} > \eta_2^{pot} \text{ and } \gamma_2 > 0 \tag{4}$$

is expected for the nematic discotic (N_D) phase ($0 < Q < 1$). One has $\gamma_1 > 0$ and $\eta_i^{pot} > 0$ in both cases. Since the kinetic contribution η_i^{kin} to the Miesowicz viscosity η_i is smaller than the potential one, the inequalities (3) and (4) are expected to hold true for the experimentally observable viscosity coefficients which are the sum of the kinetic and the potential contributions. For nematics, indeed, the inequalities $\eta_1 < \eta_3 < \eta_2$ and $\gamma_2 < 0$ are well established.[3,7] The nonequilibrium molecular dynamics simulations for nematics[1] are in accord with the relations (1, 2) and the inequalities (3). Preliminary results for a model N_D phase[8] confirmed the inequalities (4).

NONEQUILIBRIUM MOLECULAR DYNAMICS (NEMD)

The molecular dynamics simulation to be discussed here is a straightforward extension of our previous NEMD studies on fluids of nonspherical particles subjected to a plane Couette flow[1] with the (constant) shear rate $\Gamma = \partial v_x/\partial y$. So just the basic principles rather than technical details are presented here. In the simulation, Newton's equations of motion for N particles interacting with a given force law are integrated numerically (by a predictor-corrector method). Periodic boundary conditions are used. The number density $n = N/V$ is determined by N and the volume V of the periodicity box. Physical quantities of interest like the components of the pressure tensor **p** are evaluated as N-particle averages from the known positions and velocities of the particles according to the rules of statistical physics. The kinetic and potential contributions to the yx-element p_{yx} of the pressure tensor, e.g., are given by ($i = 1, 2, \ldots, N$; $j = 1, 2, \ldots, N$)

$$V p_{yx}^{\text{kin}} = m \sum_i c_y^i c_x^i, \quad V p_{yx}^{\text{pot}} = \sum_{i<j}\sum r_y^{ij} F_x^{ij} \tag{5}$$

where r^i is the position of particle "i", $c^i = \dot{r}^i - v(r^i)$ is its peculiar velocity. The relative position vector is $r^{ij} = r^i - r^j$; $F^{ij} = F(r^{ij})$ is the force acting between particles "i" and "j". The N-particle averages (5), in turn, are averaged over many thousand time steps. Division of $-p_{yx}^{\text{kin}}$ and $-p_{yx}^{\text{pot}}$ by the shear rate Γ yields the kinetic and the potential contribution to the viscosity η.

In the following, all quantities are expressed in terms of units based on the mass m of a molecule and the length and energy scales σ and ϵ provided by a Lennard-Jones (LJ) potential

$$\phi = 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right) \tag{6}$$

Thus the density n and the temperature T are in units of σ^{-3} and ϵk^{-1} where k is the Boltzmann constant; similarly the pressure, the shear rate and the viscosity are expressed in units of $\epsilon\sigma^{-3}$, $\epsilon^{1/2}m^{-1/2}\sigma^{-1}$, and $(m\epsilon)^{1/2}\sigma^{-2}$, respectively. The potential is cut off at $r = 2.5\sigma$.

In the model fluid of oriented nonspherical particles the molecular interaction potential and the pertaining forces are inferred from a Lennard-Jones ellipsoidal (LJE) potential which is generated from the spherical potential (6) by a volume conserving affine transformation. Thus the equipotential surfaces become ellipsoids of revolution with the axes ratio Q. By an appropriate choice of the scaling factors involved in the transformation, the molecular axes of the particles can be oriented in the various directions.[1] The cases with the symmetry axes parallel to the x-, y-, and z-axes are referred to as geometries "1, 2, 3".

MIESOWICZ VISCOSITIES

The results to be presented for the N_D phase are at the state point $n = 0.6$ and $T = 1.15$ (reduced LJ units) which, for a fluid of spherical particles, is close to the liquid-gas coexistence line. The pressure is ≈ 0.5. Simulation data are already available for a nematic LJE system with $Q = 7/3 \approx 2.67$. Here the axes ratio $Q = 3/7 \approx 0.43$ is chosen in order to model oblate particles. Equilibrium simulations with $Q = 3/7$, $T = 1.15$ but at densities n ranging from 0.6 to 1.15 showed that for $n \leq 1.0$, no phase transition typical for discotics (e.g. from N_D to a columnar phase) is encountered.

The equations of motion are integrated by a fifth-order Gear predictor-corrector method with the time step $\Delta t \leq 0.005$ (in LJ-units). The temperature is kept constant by rescaling the magnitude of the peculiar velocities of the particles. The Couette flow is mimicked with the homogeneous shear algorithm[9] which has been used successfully for the study of flow properties of simple fluids.[10] It has been demonstrated[11] that sufficiently accurate results can be obtained for systems with $N = 108$ particles; in the present case $N = 128$ is used. The data are extracted from simulation runs (performed on a Cray-1M) of at least 200000 time steps for each orientation and each shear rate Γ.

In Figure 1, the potential contribution (octagons) and the total (squares) Miesowicz viscosities η_1, η_2, η_3—as inferred from the yx-component of the pressure tensor—are plotted as functions of the shear rate $\Gamma = \partial v_x/\partial y$. Notice that the kinetic contribution is small but not negligible. The extrapolation to small Γ yields the desired Newtonian viscosity coefficients.

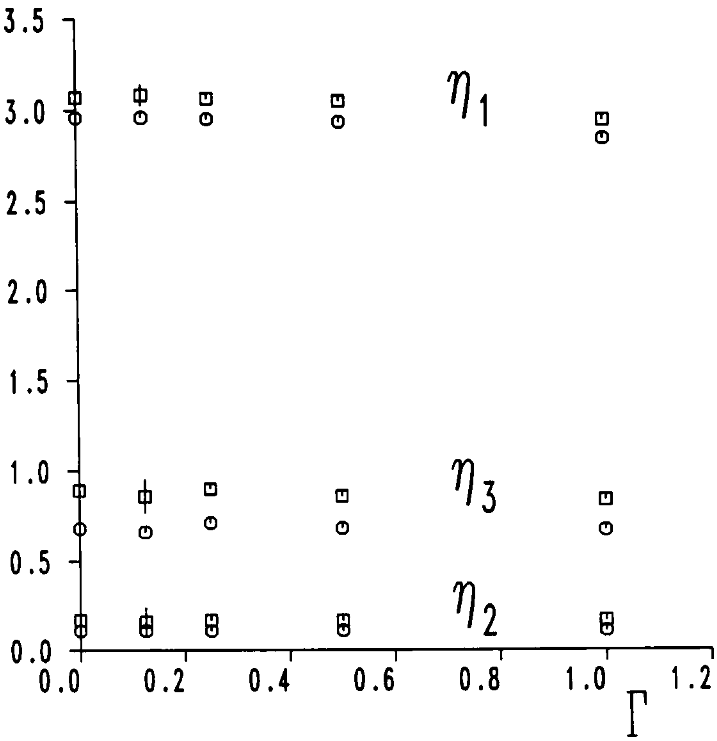

FIGURE 1 The potential contribution (octagons) and the total (squares) Miesowicz viscosities η_1, η_2 and η_3 as functions of the shear rate Γ for particles with the axes ratio $Q = \frac{3}{7}$. Typical error bars are indicated for the total viscosities at $\Gamma = 0.125$.

Clearly, there is a strong anisotropy in the viscosity coefficients. Here, η_1 (corresponding to the symmetry axis of a disk parallel to the flow direction) is the largest of all Miesowicz coefficients. For prolate particles η_1 is the smallest coefficient. The NEMD results are in reasonable agreement with the theoretical relations (1) for the potential contributions;

$$\left(\eta_3^{pot}/\eta_1^{pot}\right)^{1/2} \approx 0.47, \quad \left(\eta_2^{pot}/\eta_3^{pot}\right)^{1/2} \approx 0.41$$

have to be compared with the theoretical value $Q = 3/7 \approx 0.43$. The extrapolated (total) Miesowicz coefficients are (in LJ units)

$$\eta_1 = 3.07 \pm 0.07, \quad \eta_2 = 0.17 \pm 0.06, \quad \eta_3 = 0.89 \pm 0.09. \tag{7}$$

LESLIE COEFFICIENTS

Due to the torque acting on the particles with fixed orientation, the potential contribution to the pressure tensor contains an antisymmetric part; in particular one has $p_{yx} - p_{xy} \neq 0$ for orientations 1 and 2. The Leslie coefficients γ_1 and γ_2 can be inferred from this quantity which is also extracted from the simulation, more specifically, $p_{xy} - p_{yx}$ divided by the shear rate equals $(\gamma_1 + \gamma_2)/2$ and $(\gamma_1 - \gamma_2)/2$ for orientations 1 and 2, respectively. The resulting values for these coefficients are displayed in Figure 2 as functions of the shear rate Γ. There is also a weak non-Newtonian behavior (shear rate dependence). The extrapolated values (for small Γ) are

$$\gamma_1 = 1.96 \pm 0.09, \quad \gamma_2 = 2.90 \pm 0.09. \tag{8}$$

Notice that $\gamma_2 > 0$ in contradistinction to nematics. The Onsager-Parodi relation

$$\gamma_2 = \eta_1 - \eta_2 \tag{9}$$

is very well obeyed (within the computational accuracy) for all shear rates. From (7), e.g. one infers $\eta_1 - \eta_2 = 2.90 \pm 0.13$. The ratio $\gamma_2/\gamma_1 = 1.48$ as inferred from (8) compares quite favorably with the theoretical prediction $\gamma_2/\gamma_1 = (Q^{-2} + 1)(Q^{-2} - 1)^{-1} = 1.45$ based on (2).

CONCLUDING REMARKS

So far, all viscosity coefficients were expressed in LJ-units. For a comparison with a real substance it is preferable to present the coefficients in units of the average viscosity

$$\bar{\eta} = (\eta_1 + \eta_2 + \eta_3)/3. \tag{10}$$

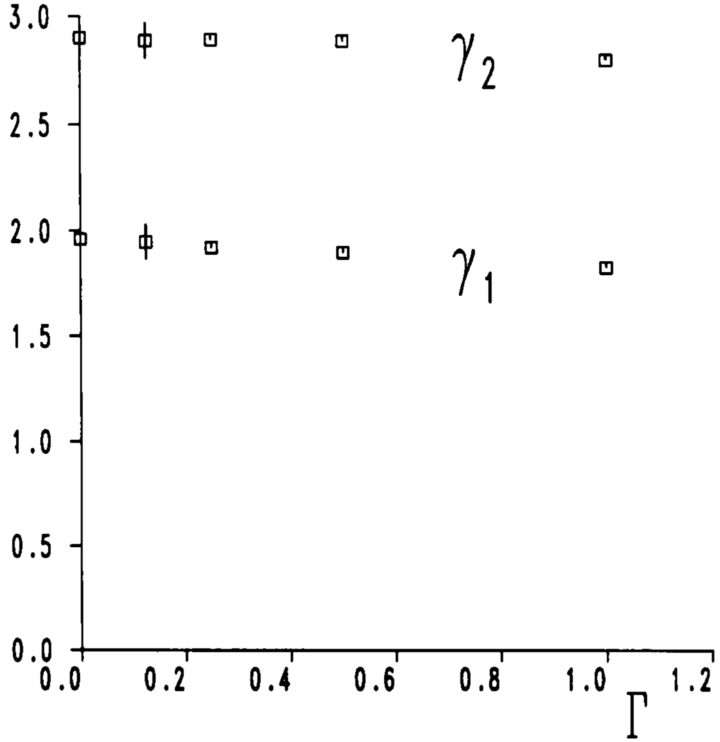

FIGURE 2 The Leslie coefficients γ_1 and γ_2 as functions of the shear rate Γ for particles with the axes ratio $Q = \frac{3}{7}$. Typical error bars are indicated at $\Gamma = 0.125$.

In Table 1 the coefficients $\eta_i^* = \eta_i/\bar{\eta}$ and $\gamma_i^* = \gamma_i/\bar{\eta}$ are listed. The values labelled by "TH^{pot}" stem from the theoretical expressions (1, 2) (with $Q = 3/7$) where only the potential contribution is taken into consideration. The results inferred from the NEMD simulation discussed before are labelled by LJE. A comparison of the analogous quantities for a fluid of prolate particles with the viscosity coefficients of nematics gave a satisfactory agreement. It is expected that the present theoretical results capture the essential features of the anisotropy of the viscosity of nematic discotics. Even if the orientation of these liquid crystals will turn out to be rather

TABLE 1

Theoretical results (potential contributions) and LJE-NEMD data for 5 reduced viscosity coefficients for particles with the axes ratio $Q = \frac{3}{7}$.

	η_1^*	η_2^*	η_3^*	γ_1^*	γ_2^*
TH^{pot}	2.46	0.08	0.45	1.64	2.38
LJE	2.23	0.12	0.65	1.42	2.11
	±0.10	±0.05	±0.10	±0.10	±0.10

difficult it should be possible to measure γ_1, the ratio γ_2/γ_1 and η_s, the viscosity in a "free" flow where no external field is applied. The viscosity η_s is related to η_1, η_2, η_{12}, γ_1 and γ_2 by

$$\eta_s = \frac{1}{2}(\eta_1 + \eta_2 - \gamma_1) + \frac{1}{4}\eta_{12}\left[1 - \left(\frac{\gamma_1}{\gamma_2}\right)^2\right].$$

The expected value for η_s is 0.40, if we take the value for η_{12} from simulations for $Q = 7/3$, assuming that this coefficient is equal for $Q = 3/7$ and $Q = 7/3$ in accordance with our theoretical prediction.[1]

In the vicinity of a transition "nematic discotic to a columnar discotic phase" the smallest Miesowicz viscosity η_2 is expected to show a pretransitional increase just as η_1 of nematics increases strongly in the vicinity of a transition "nematic to a smectic phase."[7] In both cases the order (3), (4) of the viscosity coefficients can be reversed.

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