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The flow alignment of some nematic liquid crystals

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A setup is described to determine the flow alignment angle \( \theta_0 \) in nematic liquid crystals. Results for compounds with and without a strongly polar terminal cyano group indicate that the antiparallel dipole correlation associated with cyano groups has no influence on \( \theta_0 \). The influence of the occurrence of a smectic-A phase on \( \theta_0 \) is investigated on three homologous series. The results show that \( \theta_0 \) is a very sensitive probe for smectic-like short-range order. With increasing chain lengths a decrease of \( \theta_0 \) is found, until finally no flow alignment exists anymore. Interestingly, a similar behavior is found in a homologous series without smectic phases.

I. INTRODUCTION

Nematic liquid crystals\(^1\) are anisotropic liquids in which the constituting molecules are, on average, aligned with their unique axis parallel to a preferred direction in space. This direction is labeled by the director \( \mathbf{n} \). Though a nematic liquid flows as easily as an isotropic liquid consisting of similar molecules, an analysis of the viscosities turns out to be rather complicated when the state of alignment, as given by \( \mathbf{n} \), is considered. As to be expected, the flow depends on the angle between \( \mathbf{n} \) and the flow direction and the velocity gradient, leading to the three Miesowicz viscosities \( \eta_1 \), \( \eta_2 \), and \( \eta_3 \) (see, for instance, Ref. 2 or 3). However, in addition translational motions couple to internal orientational motions, and the flow will cause the director to rotate. This behavior can be described by the hydrodynamic theory of Ericksen\(^4\) and Leslie,\(^5\) which involves in total five independent viscosity coefficients.

It is the purpose of this paper to investigate in some detail for various compounds the relation between the flow and the orientation of \( \mathbf{n} \). In the case of a simple two-dimensional shear flow (Fig. 1) and in the absence of external forces the torque density \( N \) working on \( \mathbf{n} \) is given by\(^3\)

\[
N = -(\kappa_1 \sin^2 \theta + \kappa_2 \cos^2 \theta)(\partial v/\partial x),
\]

where \( \kappa_1 \) and \( \kappa_2 \) are the shear-torque coefficients that determine the torque on \( \mathbf{n} \) when it is parallel to the velocity gradient and the velocity \( v \), respectively, while \( \theta \) is the angle between \( \mathbf{n} \) and \( v \). Equation (1) allows for an equilibrium value for which \( N = 0 \). This occurs for \( \mathbf{n} \) in the shear plane at the flow alignment angle \( \theta_0 \), determined by

\[
\tan^2 \theta_0 = -\kappa_2/\kappa_1.
\]

A real solution for \( \theta_0 \) requires the right-hand side of Eq. (2) to be positive. For many substances \( \kappa_2 \) turns out to be small negative. From thermodynamic reasons for rod-like molecules it is found that \( \kappa_1 > 0 \),\(^2\) so that small values of \( \theta_0 \) are expected. Interestingly in some substances \( \kappa_2 \) changes sign as a function of temperature, in which case no stable flow alignment exists anymore.\(^6-11\)

From the investigations to be presented it follows that any absence of flow alignment is not related to antiparallel dipole correlation of strongly polar molecules as has been suggested in the literature.\(^6,12\) In some homologous series the flow alignment angle only exists for the shorter members. The disappearance of \( \theta_0 \) can be attributed to pretransitional smectic fluctuations,\(^13,14\) leading to a divergence of \( \kappa_2 \). The flow alignment turns out to be an extremely sensitive measure for such effects, that can even be found if no smectic phase is actually observed.

In the next section first the experimental method and setup will be described. The results are given in Sec. III, while Sec. IV gives a concluding discussion. Some preliminary results have been given already in an earlier letter.\(^15\)

II. EXPERIMENTAL

Following Gähwille\(^6\) the flow alignment angle \( \theta_0 \) is determined from the change in optical path difference between the ordinary and the extraordinary component of polarized light by comparing a situation with \( \mathbf{n} \) magnetically aligned along the flow direction and one without a magnetic field, respectively. For \( \mathbf{n} \) parallel to the \( z \) axis (see Fig. 1) the optical path difference \( \Gamma_0 \) will be

\[
\Gamma_0 = (n_x - n_o)d,
\]

where \( n_o \) and \( n_x \) being the ordinary and extraordinary refractive indices, respectively, while \( d \) is the sample thickness. When \( \mathbf{n} \) makes an angle \( \theta(x) \) with the \( z \) axis, the optical path difference \( \Gamma \) will be

\[
\Gamma = \Gamma_0 + \frac{1}{2} d (n_x^2 - n_o^2) \sin 2\theta(x)
\]

FIG. 1. Flow alignment in a flat capillary, with the velocity \( v(x) \) and the angle \( \theta(x) \).
\( \Delta \Gamma = \Gamma - \Gamma_0 = [n(\theta_0) - n_0]d. \)  

(8)

With \( \theta(x) = \theta_0 \) Eqs. (5) and (8) can be combined and after some tedious rewriting one arrives at

\[
\sin^2 \theta_0 = \frac{-2(\Delta \Gamma/n_0d) - (\Delta \Gamma/n_0d)^2}{[(n_e/n_0)^2 - 1][n(\Delta \Gamma/n_0d) + 1]^2}.
\]

(9)

\( \Delta \Gamma \) can be determined experimentally from

\[
\Delta \Gamma = \lambda \Delta \delta/2\pi.
\]

(10)

where \( \lambda \) is the wavelength and \( \Delta \delta \) is the change in the phase shift \( \delta \) of the transmitted light between the situation of uniform \( n \) (\( n \parallel \nu \), using the external magnetic field) and the situation with \( n \) at \( \theta_0 \) with the flow direction \( \nu \) (field switched off).

The phase shift \( \delta \) between the ordinary and extraordinary component of the polarized light is determined with the setup shown in Fig. 2. The optical part of the setup is similar to the one used by Lim and Ho.\(^{16} \) The light beam from a He–Ne laser (\( \lambda = 632.8 \) nm) passes through a polarizer, the sample, a quarter-wave plate and a rotating polaroid before it reaches a photodiode. The polarizer is oriented at an angle of 45° with respect to the flow direction in the capillary. The quarter-wave plate is adjusted along the polarization of the incident light. This quarter-wave plate changes the elliptically polarized light from the sample back to plane-polarized light, but with the polarization direction rotated over an angle of \( \pi/2 \) with respect to the original direction. The light then passes through a rotating polaroid, that exists of a sheet of polaroid mounted on a cassette-recorder motor. The frequency \( \omega \) can be changed between 1 and 35 Hz by varying the voltage. The light intensity \( I \) after the rotating polaroid is given by

\[
I = 2I_0 \cos^2(\omega t + \delta/2) = I_0[1 + \cos(2\omega t + \delta)].
\]

(11)

The intensity of a reference beam, generated by a LED and passing through the rotating polaroid and an analyzer, is given by

\[
I_{\text{ref}} = I_0[1 + \cos(2\omega t)].
\]

(12)

The relative phase difference between the two signals is measured with a sensitive phasemeter (Bruel and Kjaer, type 2971).

The sample is placed in a high stability oven (Fig. 3). The rectangular capillary (Fig. 4) used is a modified

\[ \text{FIG. 3. Oven for flow alignment measurements; 1—connection for heating liquid, 2 and 9—glass windows, 3—hollow shield, 4 and 8—stainless steel tubes, 5—capillary, 6—copper cylinder, 7—heater, 10—connections to pressure difference system.} \]
version of a commercially obtainable flow capillary (Hellma Küvette 136-0S) with \( d = 200 \) \( \mu \text{m} \). The capillary is pressed against a copper cylinder with two channels. A pressure difference of about \( 100 \) Pa is used to drive the liquid crystal from one channel inside the cylinder through the capillary into the other channel.

The oven has a two-stage heating system. The inner stage, consisting of the copper cylinder and the sample, is heated electrically. A thermistor, which is part of an ac-Wheatstone bridge, is used for the temperature setting. A second calibrated thermistor is used to determine the temperature. The second heating stage consists of a hollow shield, through which water or oil is circulated from a constant temperature bath. Usually, the shield is about \( 1^\circ \) below the temperature of the sample. In this way it is possible to keep the sample temperature constant to better than \( 0.05^\circ \)C.

The various compounds studied and their transition temperatures are given in Tables I and II.

### III. RESULTS

In connection with the problems of the transition layers at the boundaries and in the middle of the sample first some measurements were done for N4 with \( d = 200 \) and \( 500 \) \( \mu \text{m} \), respectively. These results are given in Fig. 5 and agree well with each other.

In Fig. 6 results are given for two phenylbenzoates and two tolanes that differ in the presence or absence of a strongly polar end group, but are otherwise as similar as possible. The \( \theta_0 \) values for each of the two pairs are very much the same.

Measurements have been performed on three different homologous series, for which the higher homologs have a smectic-A phase. For the \( mAB \) series (Fig. 7) starting with 7AB no flow alignment is found anymore. This is also the case for the highest measured homolog (CPE509) of the CPE50m series. The results for these series are shown in Fig. 8. Figure 9 gives the results for the \( mCB \) series.

Finally \( \theta_0 \) has also been investigated for a homologous series without smectic phases. The results for these compounds, indicated as APAPA\( \text{m} \), are shown in Fig. 10. The trend in \( \theta_0 \) with increasing chain length is very similar to that in the previous cases.

### IV. DISCUSSION

In deriving Eqs. (7)–(9) the transition layers at the boundaries and in the middle of the sample were disregarded. In order to test this approximation experimentally, let us discuss the case that \( \theta(x) = 0 \) at \( x = \pm d/2 \) (Fig. 1).

The transition layers at the boundaries and in the middle have a thickness \( a \) and \( 2b \), respectively. Disregarding the transition layers is equivalent to assuming \( \theta = \theta_0 \) within these layers. The other limiting case is obtained by taking \( \theta = 0 \) within the layers. One then gets instead of Eq. (8)

\[
\text{FIG. 4. (a) Side view of top and lower part of the rectangular capillary; (b) Top view of the lower part of the rectangular capillary.}
\]

### TABLE I. Molecular structures of the compounds studied.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Molecular Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>mAB</td>
<td>( \text{C}<em>m\text{H}</em>{2m+1}\longrightarrow\text{N} - \text{N} - \text{C}<em>m\text{H}</em>{2m+1} )</td>
</tr>
<tr>
<td>4,4'-di-( n )-alkylazoxybenzene</td>
<td></td>
</tr>
<tr>
<td>APAPA( \text{m} )</td>
<td>( \text{CH}_3\longrightarrow\text{C} \equiv \text{N} - \text{C}<em>m\text{H}</em>{2m+1} )</td>
</tr>
<tr>
<td>Anisylidene-4-aminophenylacetate and higher homologues</td>
<td></td>
</tr>
<tr>
<td>mCB</td>
<td>( \text{C}<em>m\text{H}</em>{2m+1} \longrightarrow\text{C} \equiv \text{N} )</td>
</tr>
<tr>
<td>4-( n )-alkyl-4'-cyanobiphenyl</td>
<td></td>
</tr>
<tr>
<td>CPE50m</td>
<td>( \text{C}<em>5\text{H}</em>{11} \longrightarrow\text{O} - \text{C}<em>m\text{H}</em>{2m+1} )</td>
</tr>
<tr>
<td>4-( n )-alkoxyphenyl-trans-4-pentylcyclohexylcarboxylate</td>
<td></td>
</tr>
<tr>
<td>CPEC</td>
<td>( \text{C}<em>5\text{H}</em>{11} \longrightarrow\text{O} - \text{C} \equiv \text{N} )</td>
</tr>
<tr>
<td>4-cyanophenyl-trans-4-pentylcyclohexylcarboxylate</td>
<td></td>
</tr>
<tr>
<td>N4</td>
<td>( \text{CH}_3\longrightarrow\text{N} - \text{N} - \text{C}_4\text{H}_9 )</td>
</tr>
<tr>
<td>4-( n )-butyl-4'-methoxyazoxybenzene (mixture of both components)</td>
<td></td>
</tr>
<tr>
<td>70T</td>
<td>( \text{C}<em>7\text{H}</em>{15} \longrightarrow\text{C} \equiv \text{C} - \text{O}\text{CH}_3 )</td>
</tr>
<tr>
<td>4-heptyl-4'-methoxytolane</td>
<td></td>
</tr>
<tr>
<td>7CT</td>
<td>( \text{C}<em>7\text{H}</em>{15} \longrightarrow\text{C} \equiv \text{C} - \text{C} \equiv \text{N} )</td>
</tr>
</tbody>
</table>
TABLE II. Transition temperatures of liquid crystals studied (T_m = melting point, T_{AN} = smectic-A-nematic transition, T_c = clearing point).

<table>
<thead>
<tr>
<th>Compound</th>
<th>T_m (°C)</th>
<th>T_{AN} (°C)</th>
<th>T_c (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4AB (DIBAB)</td>
<td>15.0</td>
<td>···</td>
<td>31.9</td>
</tr>
<tr>
<td>5AB (PENTAB)</td>
<td>25.8</td>
<td>···</td>
<td>67.5</td>
</tr>
<tr>
<td>6AB (HEXAB)</td>
<td>26.0</td>
<td>17.0</td>
<td>54.2</td>
</tr>
<tr>
<td>7AB (HEBTAB)</td>
<td>34.2</td>
<td>53.9</td>
<td>70.6</td>
</tr>
<tr>
<td>APAPA1 (APAPA)</td>
<td>78.1</td>
<td>···</td>
<td>108.2</td>
</tr>
<tr>
<td>APAPA4</td>
<td>61.0</td>
<td>···</td>
<td>100.3</td>
</tr>
<tr>
<td>APAPA9</td>
<td>73.6</td>
<td>···</td>
<td>96.4</td>
</tr>
<tr>
<td>APAPA11</td>
<td>81.2</td>
<td>···</td>
<td>94.5</td>
</tr>
<tr>
<td>5CB</td>
<td>24.0</td>
<td>···</td>
<td>34.7</td>
</tr>
<tr>
<td>6CB</td>
<td>14.0</td>
<td>···</td>
<td>29.2</td>
</tr>
<tr>
<td>7CB</td>
<td>29.7</td>
<td>···</td>
<td>42.7</td>
</tr>
<tr>
<td>8CB</td>
<td>21.0</td>
<td>32.6</td>
<td>40.5</td>
</tr>
<tr>
<td>CPE301</td>
<td>41.0</td>
<td>···</td>
<td>71.8</td>
</tr>
<tr>
<td>CPE302</td>
<td>56.9</td>
<td>···</td>
<td>85.9</td>
</tr>
<tr>
<td>CPE303</td>
<td>41.2</td>
<td>···</td>
<td>71.1</td>
</tr>
<tr>
<td>CPE305</td>
<td>35.1</td>
<td>35.2</td>
<td>74.8</td>
</tr>
<tr>
<td>CPE307</td>
<td>42.1</td>
<td>57.6</td>
<td>77.4</td>
</tr>
<tr>
<td>CPE308</td>
<td>48.4</td>
<td>64.0</td>
<td>78.3-78.6</td>
</tr>
<tr>
<td>CPE309</td>
<td>52.8</td>
<td>67.0</td>
<td>75.6</td>
</tr>
<tr>
<td>CPEC</td>
<td>47.6</td>
<td>···</td>
<td>79.5</td>
</tr>
<tr>
<td>N4</td>
<td>17.0</td>
<td>···</td>
<td>73.8</td>
</tr>
<tr>
<td>7OT</td>
<td>40.2</td>
<td>···</td>
<td>51.2-52.0</td>
</tr>
<tr>
<td>7CT</td>
<td>58.5</td>
<td>···</td>
<td>65.4-66.3</td>
</tr>
</tbody>
</table>

\[ \Delta \Gamma = [n(\theta_0) - n_d](d - 2(a + b)]. \]  

(13)

In reality \( \theta \) varies over the distances \( a \) and \( b \) between the limits 0 and \( \theta_0 \), and \( \Delta \Gamma \) will be given by

\[ \Delta \Gamma = [n(\theta_0) - n_d](d - 2C(a + b)], \]  

(14)

with \( 0 < C < 1 \). From the results of Fig. 5 we note that the same \( \theta_0 \) values are found for rather different values of \( d \). This means that in Eq. (14) \( 2C(a + b) \ll d \), and that the assumption of taking \( C \approx 0 \) can be justified.

Molecules with a strongly polar CN group are well known to exhibit antiparallel dipole correlation.\(^{12, 17}\) It has been suggested that this could influence the flow alignment, eventually leading to the disappearance of \( \theta_0 \).\(^{6, 12}\) The results of Fig. 6 do not support this idea. In fact it excludes any important effect of antiparallel dipole association on the flow alignment.

From the results of the homologous series (Figs. 7–10) we note a trend of decreasing \( \theta_0 \) with increasing chain length, until finally the flow alignment disappears. Most of the compounds with this type of behavior possess a smectic-A phase. Therefore the possible influence of a smectic-A phase on the viscosities just above the smectic-A–nematic phase transition should be considered. McMillan\(^{13}\) and Jähning and Brochard\(^{14}\) predicted an increase in \( \gamma_1 = \kappa_1 + \kappa_2 \) and in \( \eta_2 \) due to the fluctuations of the local smectic order parameter above a smectic-A–nematic phase transition. This can be understood in at least a qualitative way by considering a simple shear flow and including a smectic layer structure (Fig. 11).

In the case of \( \mathbf{n} \) parallel to the velocity gradient \([\eta_1 \text{ and } \kappa_1, \text{ Fig. 11(a)}]\) the direction is parallel to the smectic layers. As the layers can move with regard to each other, in a first approximation no influence of the smectic layer structure on \( \eta_1 \) and \( \kappa_1 \) is expected. The same applies to the situation of \( \mathbf{n} \) perpendicular to the velocity and velocity gradient \([\eta_2 \text{ and } \kappa_2, \text{ Fig. 11(b)}]\) with again at most small changes of \( \eta_2 \) at the phase transition. For \( \eta_1 \) and \( \eta_3 \) this has been confirmed by measurements of Bhattacharya and Letcher.\(^{18}\) In the situation of \( \mathbf{n} \) parallel to \( \mathbf{v} \) \([\eta_3 \text{ and } \kappa_3, \text{ Fig. 11(c)}]\), the smectic layers are perpendicular to the flow direction. When there is flow the molecules have to move from one layer to another and must overcome the potential barrier associated with the layers. This leads to

![FIG. 5. Flow alignment angle \( \theta_0 \) of N4; \( \bullet \ d = 500 \mu \text{m}, \nabla \ d = 200 \mu \text{m} \).](image5.png)

![FIG. 6. Flow alignment angle \( \theta_0 \) of CPEC (\( \times \)); CPE301 (\( \bullet \)); 7OT (\( \circ \)) and 7CT (\( \nabla \)).](image6.png)

![FIG. 7. Flow alignment angle \( \theta_0 \) of the mAB series.](image7.png)
increasing and finally diverging values for $\eta_2$ and $\kappa_2$ when the phase transition is approached. For $\eta_2$ this behavior has also been found experimentally by Bhattacharya and Letcher$^{18}$ and by Kneppe$^{19}$ et al. As far as the rotational viscosities are concerned, direct measurements of $\kappa_1$ and $\kappa_2$ are not possible and we have to consider instead $\gamma_1$ and Eq. (2). The expected divergence of $\gamma_1$ near the smectic-A-nematic phase transition has been reported$^{20-23}$ From the above picture it follows that this must be due to the increase of $\kappa_2$. As away from the phase transition $|\kappa_1| \gg |\kappa_2|$ there is a strong background for $\gamma_1$ that does not diverge. On the other hand $\theta_0$ is more directly sensitive to these effects. As for rod-like nematicogenic molecules $\kappa_1$ is necessarily positive,$^2$ a change of sign of $\tan \theta_0$ is due to a change of sign of $\kappa_2$. If $\kappa_2$ increases due to presmectic fluctuations, it first changes sign from small negative values to positive ones and then diverges. This indicates that $\kappa_2$ and thus the flow alignment angle is extremely sensitive to pretransitional smectic effects. This makes the method suitable to detect the onset of presmectic fluctuations rather than the behavior close to the phase transition. In this way a presmectic increase of $\kappa_2$ might even be found without a smectic phase actually being observed. Most probably this is the reason for the disappearance of the flow alignment in CPE503 and some of the APAPA's. Believing that the experiments probe short-range smectic-like order, the question remains why in the APAPA series this does not lead to a long-range effect in the form of a phase transition to a smectic-A phase.

In principle one would like to correlate the variation of $\theta_0$ with temperature and alkyl chain length with molecular properties of the system. In the literature several theories have been given that describe the flow alignment from a molecular point of view. However, taking a somewhat closer look, the final results of the various authors turn out to be rather similar. In our discussion so far the flow alignment angle $\theta_0$ is determined by the ratio of the shear torques. In the derivation of the hydrodynamics of nematics given by Forster$^4$

$$A = \frac{3S}{2\alpha + S},$$

(15)

where

$$\alpha = \frac{I_1 + 2I_2}{I_1 - I_2},$$

(16)

in which $I_1$ and $I_2$ are the moments of inertia of the molecules parallel and perpendicular to the long axis, respectively. For $\alpha = 1$, corresponding to the limit of infinitely long molecules, this expression reduces to results found by Marrucci$^{25}$ and by Doi.$^{26}$ In the case of ellipsoidal molecules $I_1/I_2 = (W/L)^2$, where $L$ is the length and $W$ the width of the molecules, and this result has been derived earlier by Helfrich.$^{27,28}$

All these types of theory do not include any effect of presmectic fluctuations. As we have seen that $\theta_0$ is extremely sensitive to such effects it is not surprising that the results from Eq. (15) are not in agreement with
experiments. In fact this is even true for the lower members of the homologous series and for N4, in which cases presmectic effects can be expected to be least important.

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