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To cite this version:

J.P. Van Der Meulen, R.J.J. Zijlstra. Physical properties of the nematic liquid crystal, APAPA. Optical determination of the viscoelastic and elastic ratios. Journal de Physique, 1984, 45 (10), pp.1627-1642. <10.1051/jphys:0198400450100162700>. <jpa-00209904>

HAL Id: jpa-00209904
https://hal.archives-ouvertes.fr/jpa-00209904
Submitted on 1 Jan 1984

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Physical properties of the nematic liquid crystal, APAPA.
Optical determination of the viscoelastic and elastic ratios

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(Reçu le 19 décembre 1983, accepté le 24 mai 1984)

Résumé. — Nous présentons une étude des propriétés viscoélastiques et élastiques d’un cristal liquide mesuré en utilisant la technique de diffusion de la lumière laser. Les rapports entre constantes élastiques de divergence, torsion et flexion ont été déterminés ainsi que le rapport entre les paramètres de viscosité de Miłoszewicz, $\eta_1/\eta_3$, pour le nématic APAPA en fonction de la température.

Abstract. — We report a study of the viscoelastic and elastic properties of a nematic liquid crystal as measured by static and dynamic light scattering. Experimental values are reported for the splay/twist/bend elastic and visco-elastic ratio as well as for the Miłoszewicz viscosity ratio $\eta_1/\eta_3$ of APAPA in the nematic region as a function of temperature.

1. Introduction.

Nematic Liquid Crystals (NLC’s) are fluids which are translationally disordered but orientationally ordered. On average the orientation of individual molecules is parallel (or antiparallel) to a preferred direction characterized by a vector $n_0$, the nematic director. In any finite volume the instantaneous director $n(r, t)$ fluctuates around its average value $n_0$ [1].

Light scattering is caused by fluctuations of the dielectric tensor $g(r, t)$. In NLC’s the off-diagonal elements of the dielectric tensor depend linearly on the fluctuations of the director. As a consequence NLC’s exhibit strong depolarized light scattering [2].

The director fluctuations can be described by a set of linear (« hydrodynamic ») relaxation equations. It can be demonstrated that any deformation of the instantaneous director field can be expressed as a linear combination of three special types of deformation, called the splay, twist and bend distortions, each having distinct viscoelastic properties [3].

In a previous paper [2] we have described an experimental method for obtaining viscoelastic ratios of NLC’s by measuring the light scattering spectrum as a function of angle. In the present paper the techniques described in reference [2] have been applied to the compound APAPA (anisylidene-p-aminophenylacetate) in the nematic region. APAPA is a suitable material to study with the present technique since an appreciable amount of information on this compound is available for comparison. In particular, Leenhouts et al. [4, 5] studied the magnetic and optical susceptibility of this compound and its density as a function of temperature. The same authors also determined the Frank elastic constants of this material from measurements of the Freedericksz transition. The ratios of these Frank elastic constants can be compared directly with our present results. So far no viscosity data to which our data can be compared have been published for this compound; hence the results we present on these properties are new.

In our light scattering set-up (cf. Fig. 1; for details see ref. [2]) we can freely choose the scattering angle $\theta$, as well as the directions of the polarizer $i$, the analyser $f$ and the director $n_0$. In practice, one employs only a rather limited set of scattering geometries for which the light scattering results can be easily interpreted. In particular, in all convenient scattering geometries one works with either crossed or parallel polarizers while the director is chosen to be parallel or perpendicular to the scattering plane. We found it most convenient to use a scattering geometry in which the polarization of the scattered light is perpendicular to the director (« ordinary ray »), as the analysis of scattered light with the polarization of the extraordinary ray is by no means straightforward. One way to separate the
Fig. 1. — Schematic diagram of the scattering set-up. Light from the laser is polarized by the polarizer I and is scattered by the planar (P) or homeotropic (H) oriented sample. The photomultiplier tube (PMT) detects the light scattered by the sample with a direction of polarization fixed by the analyser F, and at an outside scattering angle $\theta_L$. All optical components are centred in the scattering plane A. See also figure 1 of reference [2].

Liquid Crystal Group [9]. These authors gave explicit expressions for the optical spectrum $S_E(\omega)$ of the scattered light as a function of scattering wave vector, frequency and hydrodynamic transport coefficients. From the expression for $S_E(\omega)$ given in reference [9] van Eck et al. [3, 6, 7, 10] derived an expression for the noise intensity spectrum $S_{\alpha\beta}(\omega)$:

$$S_{\alpha\beta}(\omega) = \text{const.} \cdot T^2 \left\{ \sum_{s=1,2} \frac{2 \omega u_s}{\omega^2 + (2 u_s)^2} + 2 \Gamma_1 \Gamma_2 \frac{(u_1 + u_2)}{\omega^2 + (u_1 + u_2)^2} \right\}$$

where $T$ is the absolute temperature. Two approximations were used in arriving at equation (1). The first is that only slow hydrodynamic modes need to be taken into account; this approximation is certainly satisfied in the frequency range probed by the present experiments. The second approximation is that the noise intensity spectrum $S_{\alpha\beta}(\omega)$ can be written as the auto-convolution integral of $S_E(\omega)$. This approximation is certainly satisfied if the fluctuations modulating the optical field behave as a Gaussian process. Although there is little reason a priori to assume that this is indeed the case, experiments on the photon statistics of the light scattered by some other NLC's indicate that the scattered field has Gaussian properties throughout the nematic range [11].

The spectrum $S_{\alpha\beta}(\omega)$ given in equation (1) consists of three Lorentzians, weighted by the functions $\Gamma_\alpha$. These weight-functions are given by

$$\Gamma_\alpha = G_\alpha^2 / K_\alpha(q), \quad (\alpha = 1, 2),$$

where $G_\alpha$ is a geometric factor, which depends on the orientations of the polarizer and analyser, i.e.

$$G_\alpha = \hat{e}_\alpha \cdot (i \cdot f) \cdot n_0$$

$$= f_\alpha n_\beta i_\beta + i_\alpha n_\beta f_\beta$$

$$= f_\alpha i_3 + i_\alpha f_3.$$  (3)

The vectors $i$ and $f$ stand for the chosen directions of the polarizer of the incoming light and the analyser of the scattered light respectively.

In equation (3) the vectors $i$, $f$ and $n_0$ are expressed in a coordinate system spanned by the following orthonormal base vectors $\hat{e}_3 \equiv n_0$.

$$\hat{e}_2 \equiv (n_0 \times q) / |n_0 \times q|, \quad \text{and} \quad \hat{e}_1 \equiv \hat{e}_2 \times \hat{e}_3.$$  (4)

The vector $q$ is the wave vector characterizing a particular director deformation mode. The relation between the wave vector $q$ and the scattering angle $\theta$ depends on the polarizations of incident and scattered light. Expressions for $q$ as a function of $\theta$ for different scattering geometries are summarized in table I. The unit vector $n_0$ stands for the time-averaged nematic director. The free energy due to a particular director deformation is given by:

2. Theory.

A hydrodynamic theory for light scattering by nematic liquid crystals was first worked out by the Orsay
Table I. — Set of optical configurations to be considered, as pointed out in the text.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Conditions</th>
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<tbody>
<tr>
<td></td>
<td>1) $G_1$</td>
</tr>
<tr>
<td>$[I \perp] [P \perp] [F \parallel]$</td>
<td>$\neq 0$</td>
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<tr>
<td>$[I \perp] [P \perp] [F \parallel]$</td>
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<td>$[I \parallel] [P \perp] [F \parallel]$</td>
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<tr>
<td>$[I \parallel] [P \parallel] [F \parallel]$</td>
<td>$1$</td>
</tr>
<tr>
<td>$[I \perp] [H \parallel] [F \parallel]$</td>
<td>$0$</td>
</tr>
<tr>
<td>$[I \perp] [H \parallel] [F \parallel]$</td>
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<tr>
<td>$[I \parallel] [H \parallel] [F \parallel]$</td>
<td>$0$</td>
</tr>
<tr>
<td>$[I \parallel] [H \parallel] [F \parallel]$</td>
<td>$1$</td>
</tr>
</tbody>
</table>

Explanation:
- $[I \perp]$ means: polarizer $\perp$, $/\parallel$ to plane $A$ (see fig. 1).
- $[F \parallel]$ means: analyzer $\parallel$, $/\parallel$ to $A$.
- $[P \perp]$ means: planar oriented NLC-sample with director $n_0 \perp$, $/\parallel$ to $A$ and $/\parallel$ to incident light beam.
- $[H \parallel]$ means: homeotropic oriented NLC-sample with director $n_0 /\parallel$ to $A$ and $/\parallel$ to incident light beam.

Notes:
- $G_1, G_2$ are optical parameters: $G_n = n_s f_s + n_f f_f$ (cf. Eq. (3)).
- $n_1, n_2$ are refractive indices; subscripts $\perp, /\parallel$ denote that the direction of polarization of the light beam is $\perp, /\parallel$ to $n_0$, respectively.
- $q$ is the scattering wave vector: $q = k_i - k_f$, where $k_i, k_f$ are the wave vectors of the incident and scattered light respectively.
- $\theta$, $\theta_L$ are the scattering angles (inside and outside NLC), respectively.

Note: the relation between $\theta$ and $\theta_L$ is given by Snell's law.

Notes:
- $G_1^2 = n_1^2 \sin^2 (\theta) (n_1^2 + n_1^2 - 2 n_1 n_2 \cos (\theta))$; $G_2^2 = 1 - G_1^2$.
- $G_2 (\theta) \rightarrow 0$ for $\theta \lesssim 3^\circ$.
- $q_1 = (\omega_0/c)(n_1 - n_2 \cos (\theta))$, $q_{11} = q_1$.
- $q_2 = (\omega_0/c)(n_1 - n_2 \cos (\theta))$, $q_{22} = q_2$.
- $G_1^2 = \sin^2 (\theta)$, $q_{11} = q_1$.
- $G_2^2 = \sin^2 (\theta)$, $q_{22} = q_2$.
- $q_{11}, q_{22}$ are defined as in (e).

Cartesian base system introduced below equation (3), the expression for the free energy takes a diagonal quadratic form in the Fourier transforms $\delta n(q)$ of the director fluctuations (see Ref. [2]). One has:

$$F_d = \frac{1}{2} \int_V dr [K_1 (V \cdot n(r))^2 + K_2 (n(r) \cdot V \times n(r))^2 + K_3 (n(r) \cdot V \times n(r))^2],$$

where $K_i (i = 1, 2, 3)$ are the Frank elastic constants for splay, twist and bend respectively. Using the

$$F_d = \frac{1}{2} V \sum_{q} \sum_{s=1,2} \delta n_s^2 (q) \cdot K_s (q),$$

where $K_i (i = 1, 2, 3)$ are the Frank elastic constants for splay, twist and bend respectively. Using the
where 
\[ K_\alpha(q) = K_\alpha q^2 + K_3 q^2. \]  
(6)

$q_{\parallel}$ stands for the component of $q$ parallel to $n_0$ while $q_\perp = q - q_{\parallel}$.

In this coordinate frame the transport equations for the director fluctuation modes also reduce to a particularly simple form:

\[ \frac{\partial}{\partial t} \delta n_\alpha(q) + \frac{1}{\tau_\alpha} \delta n_\alpha(q) = 0 \quad (\alpha = 1, 2), \]  
(7)

where it has been assumed that $\delta n_\alpha(q) \ll 1$ [9, 2].

$\tau_\alpha$ in equation (6) is given by [9]

\[ \tau_\alpha(q) = \left( \frac{\eta^{\text{eff}}_\alpha}{K_\alpha} \right) \]  
(8)

with

\[ \eta^{\text{eff}}_\alpha(q) = \gamma_1 - \frac{(\alpha_3 q_\|^2 - \alpha_2 q_\perp^2)^2}{\eta_2 q_\|^2 + (\eta_1 + \eta_1 + \eta_1) q_\perp^2 + \eta_1 q_\perp^2}, \]  
(9)

\[ \eta^{\text{eff}}_2(q) = \gamma_1 - \frac{\alpha_3 q_\|^2}{\eta_3 q_\perp^2 + \eta_1 q_\perp^2}. \]  
(10)

The widths of the Lorentzians in equation (1) are expressed in terms of relaxation rates $\eta_\alpha (\alpha = 1, 2)$. These relaxation rates are related to the $\tau_\alpha$ in equation (7) by $\eta_\alpha = \tau_\alpha^{-1}$. The viscosity terms $\gamma_1$ and $\eta_1$ occurring in equations (9, 10) can be expressed in terms of Leslie coefficients $\alpha_i$ [12]

\[ \gamma_1 = \alpha_3 - \alpha_2, \]  

\[ \gamma_1 = \frac{1}{2} (\alpha_2 + \alpha_4 + \alpha_5), \]  

\[ \eta_2 = \frac{1}{2} (\alpha_3 + \alpha_4 + \alpha_6), \]  

\[ \eta_3 = \frac{1}{2} \alpha_4, \]  

\[ \eta_{12} = \alpha_1. \]  
(11)

Of course, equations (9, 10) could have been written exclusively in terms of Leslie coefficients; this however would have resulted in rather bulky expressions. In writing down the more compact relations equations (9, 10) we have made use of the Onsager Parodi relation $\gamma_2 \equiv \alpha_2 + \alpha_3 = \alpha_6 - \alpha_3 = \eta_2 - \eta_3$ [13]. We shall now briefly discuss the meaning of the coefficients $\alpha, \gamma$ and $\eta$ occurring in equations (9, 10).

The Leslie coefficients $\alpha_i (i = 1, ..., 6)$ are the fundamental transport coefficients that occur in the constitutive relation for the viscous stress tensor of an uniaxial fluid:

\[ \sigma_{\alpha \beta} = \alpha_1 n_\alpha n_\beta n_\mu n_\mu A_{\alpha \beta} + \alpha_2 n_\alpha N_{\alpha \beta} + \alpha_3 n_\beta N_\alpha + \alpha_4 A_{\alpha \beta} + \alpha_5 n_\alpha n_\mu A_{\mu \beta} + \alpha_6 n_\beta n_\mu A_{\mu \alpha}, \]  
(12)

(summation according to Einstein convention; Cartesian components are indicated by Greek subscripts).

In equation (12) $A$ stands for the symmetric part of the velocity-gradient tensor, and $N$ is given by

\[ N_\alpha = \frac{d n_\alpha}{d t} - \mathbf{W}_{\alpha \beta} \eta_\beta \]  
(13)

where $\mathbf{W}$ represents the antisymmetric part of the constitutive velocity-gradient tensor. Note that the term with $\alpha_4$ is independent of the director $n_0$. The shear torque coefficients $\gamma_1 (i = 1, 2)$ occur in the equation for the viscous torque density:

\[ \mathbf{\Gamma}_{\text{visc}} = - \gamma_1 n \times N - \gamma_2 n \times \mathbf{A} \cdot n. \]  
(14)

$\gamma_1$ is commonly referred to as the rotational viscosity. Note that all Leslie coefficients have the same dimension as the viscosity. Equations (11) relate the Leslie coefficients to another set of viscosity coefficients that is often used, particularly in the description of shear flow experiments on uniaxial fluids, the so called Mieòwicz coefficients $\eta_\alpha (\alpha = 1, 2, 3)$ [8, 14-17]. The different Mieòwicz coefficients describe the effective shear viscosity of a nematic fluid for different flow geometries. In particular (cf. Fig. 2):

\[ \eta_1 \] corresponds to the case: $n_0 \parallel v, \quad n_0 \parallel v$

\[ \eta_2 \] —

\[ \eta_3 \] —

\[ n_0 \perp v, \quad n_0 \perp v \]

Fig. 2. — Viscosity and shear-torque coefficients of an aligned nematic as measured in a shear flow experiment, $n_i$ and $K_i (i = 1, 2, 3)$, and their relations to the Leslie coefficients, $\alpha_i (i = 1, ..., 6)$.

Finally we have to mention the viscosity coefficient $\eta_{12} = \alpha_1$ (see Eq. (9)) which occurs naturally in the description of shear flow experiments where $n_0$ makes an angle with $v$ of between $0^\circ$ and $90^\circ$. As is clear from equations (9, 10) light scattering experiments can be expected to yield information on certain combinations of Leslie coefficients.

From equations (9, 10) it follows that $\eta^{\text{eff}}(q)$ depends on the ratio of $q_{\parallel}/q_{\perp}$, but is independent of the magnitude $q \equiv |q|$. The relaxation rates $\eta_\alpha = K_\alpha/\eta^{\text{eff}}(q)$ depend strongly on the magnitude of $q$ as $K_\alpha$ is a quadratic function of $q_{\parallel}, q_{\perp}$. The expressions for the viscosity coefficients $\eta^{\text{eff}}_\alpha$ take simpler forms for...
those special configurations where either \( q = 0 \) or \( q_\parallel = 0 \) (cf. Fig. 3). In the situation where \( q \) is along the director, \( q_\perp = 0 \), the two modes consist only of pure bend distortions, i.e. \( u_{s1} = u_{s2} = u_{\text{bend}} \). Then \( \eta_{\text{eff}}(q) \) reduces to:

\[
\eta_{\text{eff}}^1(q; q_\perp = 0) = \eta_{\text{eff}}^2(q; q_\perp = 0) = \gamma_1 - \alpha_2/\eta_1 \equiv \eta_{\text{bend}},
\]

(15)

and we have:

\[
K_1(q; q_\perp = 0) = K_2(q; q_\perp = 0) = K_{\text{bend}} \cdot q_\parallel^2
\]

(16)

Fig. 3. — The two uncorrelated fluctuation modes \( \delta n_1 \) and \( \delta n_2 \). The base \( \hat{e}_1, \hat{e}_2, \hat{e}_3 \) is defined in such a way that \( \hat{e}_3 = \hat{n}_0 \) and \( \hat{e}_2 \perp q \), hence \( q_\parallel = 0 \). If \( q \not/ \parallel \hat{n}_0 \), then \( \delta n_1 \) and \( \delta n_2 \) are due to pure bend distortions; if \( q \perp \hat{n}_0 \), then \( \delta n_1 \) and \( \delta n_2 \) are due to pure splay and pure twist distortions respectively.

In the situation where \( q \) is perpendicular to the director, \( q_\parallel = 0 \), the bend/splay mode becomes pure splay, \( u_{s1} = u_{\text{splay}} \), while the bend/twist mode becomes pure twist, \( u_{s2} = u_{\text{twist}} \). Then \( \eta_{\text{eff}}(q) \) reduces to:

\[
\eta_{\text{eff}}^1(q; q_\parallel = 0) = \gamma_1 - \alpha_2/\eta_1 \equiv \eta_{\text{splay}},
\]

(17)

\[
\eta_{\text{eff}}^2(q; q_\parallel = 0) = \gamma_1 \equiv \eta_{\text{twist}},
\]

(18)

while:

\[
K_1(q; q_\parallel = 0) = K_1 \cdot q_\parallel^2 = K_{\text{splay}} \cdot q_\parallel^2,
\]

(19)

\[
K_2(q; q_\parallel = 0) = K_2 \cdot q_\parallel^2 = K_{\text{twist}} \cdot q_\parallel^2.
\]

(20)

It should be noted that, as NLC’s are birefringent, it is impossible to have depolarized light scattering with both \( q_\parallel \) and \( q_\perp \) equal to zero. This is because the length of \( k_\parallel \) is not equal to the length of \( k_\perp \). At \( \theta = 0^\circ \) the scattering wave vector \( q = (\omega_0/c) (n_\parallel - n_\perp) \), which is generally far from negligible.

Equations (15-20) suggest that it is possible to determine the ratio of the elastic and viscosity coefficients, due to pure splay, pure twist or pure bend distortions, by using an optical configuration, where either \( q_\parallel = 0 \) or \( q_\perp = 0 \). In the configuration where \( q_\parallel = 0 \), both modes become degenerate and become purely of the « bend » type. In all other configurations, however, \( S_{\text{eff}}(\omega) \) of equation (1) will consist of a sum of Lorentzians due to the two modes. In practice it turns out that the half-bandwidths of these Lorentzians are of the same order of magnitude. Therefore it will in general not be possible to distinguish the separate contributions to the spectrum \( S_{\text{eff}} \), measured at an arbitrary scattering angle.

However, because these Lorentzians are weighted by the functions \( F_{\text{eff}} \), one might try to choose an optical arrangement such that the scattering intensity due to one particular mode is much stronger than the others. For the scattering configurations that could be realized with our experimental set-up, we were never able to reach a situation where one mode truly dominates the others. Therefore we did not attempt to measure isolated modes. We decided instead to perform measurements over a wide range of scattering angles and to deduce the viscoelastic ratios of interest by computer fitting theoretical relations equations (1-10) to the experimental data.

In the next section we discuss in somewhat more detail our reasons for choosing this approach.

3. Synopsis of suitable optical configurations.

In order to measure only pure splay, twist or bend in a straightforward manner the following four conditions have to be met:

1) If one wishes to observe one single mode (\( \alpha = 1 \) or 2), one of the factors \( G_1 \) or \( G_2 \) must be zero, but not both.

2) In order to determine the physical quantities connected with pure splay, twist or bend distortions, either \( q_\parallel \) or \( q_\perp \) must be zero.

3) In order to minimize stray light one must use crossed polarizers.

4) Since nematics are highly anisotropic, they show birefringence. Lax and Nelson [18] and Langevin and Bouchiat [19] have pointed to the necessity of making extra corrections to the expressions for the static light scattering intensity in the case of measurements of the so-called extraordinary part of the scattered light (i.e. light with a polarization component parallel to the director) (cf. Ref. [2]). Therefore to avoid such corrections one must measure only the ordinary part of the scattered light by making the analyser perpendicular to the director.

We shall now proceed to show that for the measurements of scattering by one single mode the four
conditions mentioned cannot be satisfied simultaneously. It will however prove possible to find optical configurations which satisfy conditions 1, 3 and 4 or 2, 3 and 4. Such configurations will be discussed in some detail.

Let us begin by considering condition 2. The configuration for which \( q_\| = 0 \) or \( q_\perp = 0 \) corresponds to the case where the director \( n_0 \) is parallel or perpendicular to the scattering plane \( A \). Condition 1 can then be satisfied only in those cases where the polarizer \( i \) and analyzer \( f \) are parallel or perpendicular to \( A \). In the case where \( n_0 \) is parallel to \( A \), the angle between \( n_0 \) and \( k_i \) is in principle variable. In practice we can restrict our attention to the case where \( n_0 \) is either parallel or perpendicular to \( k_i \), since the effect of changing the angle between \( k_i \) and \( n_0 \) can also be achieved by changing the scattering angle \( \theta \). The case for which the director is perpendicular to \( k_i \) can be achieved by using a sample with the director parallel to the glass walls (uniformly planar sample). The case for which the director is parallel to \( k_i \) is most easily realized with a sample where the director is perpendicular to the glass walls (homeotropic sample). We can therefore limit the discussion to the following optical configurations:

a) \( i \perp A \), indicated by \([ I \perp]\) or \( i \parallel A \); \( [I \parallel] \);
b) \( f \perp A \); \( [F \perp] \) or \( f \parallel A \);

The symbols in brackets \([ , ]\) are related to these conditions and are defined for convenience. In table I the different experimental configurations are summarized. All in all there are 12 distinct configurations; (2 of a) \times (2 of b) \times (3 of c). However, not all experimental configurations that belong to this set satisfy conditions 1), 2), 3) and 4). By inspection of table I it is possible to see which configurations are compatible with conditions 1)-4) mentioned above.

The angular distribution of the average intensity of the scattered light, i.e. the differential cross section \( d\sigma \) per solid angle \( d\Omega \), is given by [6, 7, 10]:

\[
\frac{d\sigma}{d\Omega} = \text{const.} \cdot T \cdot \sum_{a=1,2} \Gamma_a
\]

\[
= \text{const.} \cdot T \cdot \sum_{a=1,2} G^2_a(K_a q_\parallel^4 + K_3 q_\perp^4) \quad (21)
\]

As can be seen from table I there are five configurations for which \( G_1 = G_2 = 0 \). As a consequence no light scattering due to director fluctuations will be observed in these cases. Note that in the other cases considered in table I the conditions that only one of the factors \( G_a = 0 \) while at the same time only \( q_\parallel \) or \( q_\perp \) is non-zero are met only for certain special scattering angles. In addition we note that there are only two cases left, which satisfy the conditions 3) \((i \perp f)\) and 4) \((f \perp n_0)\) and where only one of the \( G_a \)'s is non-zero.

We can divide the set of configurations of table I into three types, two with planar oriented samples (cf. Table I with \([P \perp]\) and \([P \parallel]\) and one with homeotropic oriented samples (cf. Table I with \([H \parallel]\)).

With the first type (Table I with \([P \perp]\)) no bend distortions will contribute to the light scattering intensity, because \( q \perp n_0 \) and hence \( q_\perp = 0 \). Only a mixture of pure splay and pure twist distortions will be observed.

The second type (Table I with \([P \parallel]\)) has two configurations, indicated by \([I \perp]\) \([P \parallel]\) \([F \perp]\) and \([I \parallel]\) \([P \parallel]\) \([F \perp]\), \( G_1 = 0 \), which implies that only distortions of the twist/bend-mode (\( x = 2 \)) are observed. With the configuration indicated by \([I \perp]\) \([P \parallel]\) \([F \perp]\) only splay/bend distortions are observed, since \( G_2 = 0 \). There are no configurations of this type where the component \( q_\parallel \) or \( q_\perp \) will be zero, except at a special scattering angle in configuration \([I \perp]\) \([P \parallel]\) \([F \parallel]\) where \( q_\perp = 0 \). Because in this particular case only pure bend distortion is observed, this angle is called the bend-angle. A more detailed study of configuration \([I \perp]\) \([P \parallel]\) \([F \parallel]\) is reported by van Eck et al. [6, 3]. For most nematics this bend-angle is rather large (\( \theta \approx 40^\circ \)). At such large scattering angles the scattered intensity is low and \( S_{\alpha\beta} \) cannot be measured very accurately. In addition condition 4) is not fulfilled.

The configurations of the third type which requires homeotropic samples (Table I with \([H \parallel]\)) yield no new information that could not be determined with planar samples.

In summary we can conclude that in the case of every configuration listed in table I it is impossible to single out the contribution of only one type of distortion, except in the case of the bend mode, in which case the scattering angle is too large to be of practical use. It is for this reason that we decided not to use the single mode method.

The contribution of each type of distortion can be varied by changing the scattering angle \( \theta \). This can easily be understood because the geometrical factors \( \Gamma_a \) in equation (1) are related to \( \theta \). Moreover, as a variation of \( \theta \) implies a variation of the scattering wave vector \( q \), the effective viscosity \( \eta_\text{eff}(q) \) and elasticity \( K_\alpha(q) \) are also subject to variation (cf. Eqs. (6, 9, 10)). Hence changing the scattering angle should have a pronounced effect on both the shape and the intensity of the noise intensity spectrum. Below we indicate how information about the viscoelastic properties of nematics can be obtained from a computer fit to the scattering data over a range of scattering angles.
According to table I there are seven configurations left for investigation, because for the other five configurations it holds that $G_1 = G_2 = 0$. These seven configurations are:

i) type $[P \perp]$ : configurations $[I \perp] [P \perp] [F \perp]$ and $[I \perp] [P \perp] [F \perp]$ (splay/twist mixtures),

ii) type $[P \neq]$ : configurations $[I \perp] [P \neq] [F \perp]$, $[I \perp] [P \neq] [F \perp]$ (twist/bend mixtures), and $[I \perp] [P \neq] [F \perp]$ (splay/bend mixtures),

iii) type $[H \neq]$ : configurations $[I \perp] [H \neq] [F \perp]$ (twist/bend mixtures) and $[I \perp] [H \neq] [F \perp]$ (splay/bend mixtures),

where the nomenclature of table I is used. Note that the conditions 3) (i 1 f) and 4) (f 1 no) are only fulfilled for the configurations $[I \perp] [P \perp] [F \perp]$ and $[I \perp] [P \perp] [F \perp]$. Only two of the three types of distortions will contribute to the light scattering in any of these seven configurations.

We use a fitting procedure to single out the contributions of each individual distortion. In order to obtain accurate results it is necessary for the ratio of these contributions to change sufficiently as the scattering angle is varied.

The minimum and maximum angles attainable are limited by the experimental set-up. At small angles (0 < 30°) the scattered light is mixed with unscattered light (heterodyne admixture, see Ref. [2]). At large angles (0 > 30°) it turned out that, in order to detect an appropriate relative excess noise [10], the incoming laser light must be so intense that it will give rise to appreciable heating of the NLC.

The maximum angle is also limited by the dimension of « conventional » sample holders. This imposes an absolute upper limit of $\theta_{max} \approx 30^\circ$ upon the scattering angles. The relative contributions of the different distortion types vary as the scattering angle is changed from $\theta_{min}$ to $\theta_{max}$. This angle dependence is discussed in a more quantitative fashion in the following sections, where the preferred scattering configurations are selected for the angle-dependent light scattering experiments. In addition the numerical procedures are described which are used to extract the ratios of the elastic constants and viscosity coefficients from the experimental data.

3.1 SPLAY-TWIST MIXTURES. — (cf. table I with configurations $[I \perp] [P \perp] [F \perp]$ and $[I \perp] [P \perp] [F \perp]$).

For the configurations $[I \perp] [P \perp] [F \perp]$ and $[I \perp] [P \perp] [F \perp]$ (cf. Table I) the contributions of the splay and twist distortions to $S_{A1}$ depend only on the values of $G_1$ (see Eq. (1)). The indices $\alpha = 1$ and $\alpha = 2$ stand here for the splay and twist distortions respectively. We can define a quantity $x$:

$$x \equiv \frac{G_1 - G_2}{G_1 + G_2},$$

such that $x = -1$ corresponds to pure twist and $x = 1$ corresponds to pure splay. For these configurations $q_1 = 0$. Consequently $K_{s}(q) = K_{s} q_{2}^{2}$. With the help of equation (2) one obtains:

$$x = \frac{G_1 - \left(\frac{K_{s}}{K_{t}}\right) G_2}{G_1 + \left(\frac{K_{s}}{K_{t}}\right) G_2}.$$

Hence the angle dependence of $x$ contains the known geometrical factors $G_1$ and the a priori unknown ratio $K_{s}/K_{t}$. However, $K_{s}/K_{t}$ can be measured by light scattering.

An example of the angle dependence of $x$ is shown in figure 4 (indicated by A). For this example we have chosen $K_{s}/K_{t} = 1.5$, a typical value for the nematic APAPA. We have also used typical values for the ordinary and extraordinary refractive indices $n_1 = 1.5$ and $n_2 = 1.7$. Other reasonable choices for these parameters lead to very similar plots of $x$ vs. $\theta$.

It follows from figure 4 (case A) that using configurations $[I \perp] [P \perp] [F \perp]$ and $[I \perp] [P \perp] [F \perp]$ (cf. Table I) the ratio of the contributions due to the splay and to the twist distortions changes sufficiently over the range of scattering angles with $0^\circ < \theta < 30^\circ$. Of these two configurations configuration $[I \perp] [P \perp] [F \perp]$ is preferred because it satisfies conditions 3) and 4) (cf. Table I). Using this configuration the detected noise intensity spectrum (cf. Eq. (1)) consists
of three Lorentzians weighted by factors which are related to \( \Gamma_v \). The half-bandwidths of all these Lorentzians are reduced, since they are proportional to \( q_1^2 \) (cf. Eqs. (6, 17-20)) because \( q_\parallel = 0 \).

Previous experiments using configuration [1, 7] [P, 7] [F // 7] (see Refs. [2, 6, 7, 9]) had shown that the half-bandwidths of the three Lorentzians are of the same order of magnitude [2, 20]. Hence, they cannot be disentangled from one spectrum. Therefore the following procedure is used. The experimental spectra are most conveniently compared with theoretical line-shapes by focussing attention on the position of the maximum of the spectrum multiplied by \( \omega \), i.e. the maximum of the function

\[
\tilde{s}(\omega) = \omega S_{\alpha}(\omega) . \tag{24}
\]

For a pure Lorentzian the maximum \( \omega_m \) of \( \tilde{s}(\omega) \), defined by

\[
\left( \frac{\partial \tilde{s}(\omega)}{\partial \omega} \right)_{\omega = \omega_m} = 0 , \tag{25}
\]

coinsides with the half-bandwidth.

For a sum of Lorentzians the half-bandwidth can of course be measured but it is not related in a simple way to any theoretical quantity. In contrast the comparison of \( \omega_m \), for a sum of Lorentzians with the corresponding theoretical quantity is still relatively straightforward.

If we substitute equation (1) into equation (25) we obtain

\[
G_1^4 \left( \frac{K_1}{\eta_{\text{play}}} \right) \left[ \frac{2 K_1}{\eta_{\text{play}}} q_1^2 - \omega_m^2 \right] + G_2^4 \left( \frac{K_1}{K_2} \right) \left( \frac{K_2}{\eta_{\text{twist}}} \right) \left[ \frac{2 K_2}{\eta_{\text{twist}}} q_1^2 - \omega_m^2 \right] + G_1^2 G_2^2 \left( \frac{K_1}{\eta_{\text{play}}} + \frac{K_2}{\eta_{\text{twist}}} \right) \left( \frac{K_1}{\eta_{\text{play}}} + \frac{K_2}{\eta_{\text{twist}}} \right) q_1^2 - \omega_m^2 \right] = 0 . \tag{26}
\]

This equation contains the known variables \( G_1^2 \), \( G_2^2 \), \( q_1^2 \) and \( \omega_m \), and the unknown \( \eta_{\text{play}}/K_1 \), \( \eta_{\text{twist}}/K_2 \) and \( K_1/K_2 \). Note that \( K_1/K_2 \) can be obtained from a measurement of the angular distribution of the scattered light [2] by using the same configuration.

A good impression of how \( \omega_m \) can be determined is given by figure 5, which shows a typical spectrum \( S_{\alpha} \). Measurements of the angular dependence of the spectral noise intensity \( S_{\alpha}(\omega) \) yield a set of \( \omega_m \)- and \( q_1^2 \)-values with the corresponding equations of the form (26). Now we use a computer procedure to find the values for the viscoelastic and elastic ratios that fit best to the set of equations (26). It turned out that this procedure is not sensitive to any particular choice of starting values. Figure 6 shows a typical plot of \( \omega_m \) versus \( q_1^2 \). The solid line is a computer fit using equation (26). The fitting procedures allow for a relative error of 2 \( \% \) for the viscoelastic ratios. If we use \( K_1/K_2 \) as a fitting parameter, the estimated error in \( K_1/K_2 \) is about 30 \( \% \) which is rather large [21].

One can understand the cause for this rather large error by considering figure 7. In this figure two theoretical curves are plotted, calculated with the same viscoelastic ratios but for two values for \( K_1/K_2 \) which are 50 \( \% \) apart. Obviously the two curves differ from each other by not more than 2 \( \% \) which equals the experimental error in the measured values of \( \omega_m \). However, there is no need to use \( K_1/K_2 \) as a fitting parameter, as \( K_1/K_2 \) can also be obtained with an experimental error of about 2 \( \% \) from mea-
Fig. 6. — Example of measured data of $\omega_m$ versus the square of the scattering wave vector, $q_1^2$. The curve is the best computer fit to these data (cf. Eq. (26)).

Fig. 7. — The half-band width of the scattered light plotted versus $q_1^2$ ($q =$ scattering wave vector). Two curves are plotted with different values for $K_1/K_2$, curve 1 with $K_x/K_y = 2$, curve 2 with $K_x/K_y = 3$. Other typical values chosen are $n_{s} = 1.5, n_1 = 1.65, \eta_{splay}/K_1 = 6 \times 10^9$ sm$^{-2}$, $\eta_{twist}/K_2 = 9 \times 10^9$ sm$^{-2}$. Obviously $1/2 \omega_m$ is rather independent of the values for $K_1/K_2$.

3.2 BEND-TWIST MIXTURES. — (cf. table I with configurations $[I \perp] [P \perp] [F \perp], [I \perp] [P \perp] [F \perp]$, and $[I \perp] [H \perp] [F \perp]$).

In the case of configurations $[I \perp] [P \perp] [F \perp], [I \perp] [P \perp] [F \perp]$ and $[I \perp] [H \perp] [F \perp]$ (cf. Table I) only one mode ($\alpha = 2, \Gamma = 0$) contributes to $S_{A1}$. Pure Lorentzian line broadening will be observed, because only one term is left in equation (1). The single relaxation time $\tau$, which is determined for this spectrum at a certain scattering angle, can be written as a function of $q_1$ and $q_{1\parallel}$ and of the bend and twist viscoelastic ratio (cf. Eqs. (8, 10)). In these cases we have defined a quantity $x'$ by:

$$x' \equiv \frac{q_1^2 - q_{1\parallel}^2}{q_1^2 + q_{1\parallel}^2}. \tag{27}$$

Note that $x'$, like $x$, varies between $-1$ and $1$. In the limiting case $q_{1\parallel} = 0$ (pure twist; cf. Eqs. (18, 20)), one has $x' = 1$. In the pure bend limit ($q_1 = 0$; cf. Eqs. (15, 16)) $x' = -1$. Figure 4 (B, C, D) shows the angle dependence of $x'$ for the configuration $[I \perp] [P \perp] [F \perp], [I \perp] [P \perp] [F \perp]$ and $[I \perp] [H \perp] [F \perp]$. To calculate $x'$ we used the same values of $n_1$ and $n_{s}$ as for $x$ (Fig. 4 with A). From figure 4 it follows that the variable $x'$ shows large variations for the configurations $[I \perp] [P \perp] [F \perp]$ (case B) and $[I \perp] [P \perp] [F \perp]$ (case C), but not for configuration $[I \perp] [H \perp] [F \perp]$ (case D). Although configuration $[I \perp] [P \perp] [F \perp]$ gives a larger variation of $x'$ than does configuration $[I \perp] [P \perp] [F \perp]$, we opted for configuration $[I \perp] [P \perp] [F \perp]$ because it satisfies conditions 3) and 4). (For a more detailed description of configuration $[I \perp] [P \perp] [F \perp]$ cf. Refs. [6, 3].) Configuration $[I \perp] [P \perp] [F \perp]$ is shown schematically in figure 8. Because, in this configuration, $G_1 = 0$

Fig. 8. — Diagram of the experimental configuration for a bend/twist mode measurement (configuration $[I \perp] [P \perp] [F \perp]$, cf. Table I).

measurements of the angular distributions of the scattered light, as stated before. We therefore fitted our data using as input this more accurate value for $K_1/K_2$. The method used to obtain $K_1/K_2$ from the angle dependence of the static light scattering intensity in configuration $[I \perp] [P \perp] [F \perp]$ is described in some detail in reference [2].

In summary we conclude that using configuration $[I \perp] [P \perp] [F \perp]$ it is possible to obtain the splay and twist viscoelastic ratios as well as the splay/twist elastic ratio.

only information arising from bend-twist distortions can be obtained. Since only one Lorentzian is left in equation (1), the measured half-band width $(\Delta \omega_{1/2})_{\text{exp}}$ of $S_{A1}$ is equal to

$$(\Delta \omega_{1/2})_{\text{exp}} = \omega_m = 2 \omega_{2\parallel}. \tag{28}$$

Note that with configuration $[I \perp] [P \perp] [F \perp]$ the two types of distortion do not give rise to different Lorentzians in contrast with configuration $[I \perp] [P \perp] [F \perp]$, but they both contribute with variable weight to the half-band width $\omega_{2\parallel}$. In order to extract the bend and twist distortion properties, we must
follow a procedure different from the one described in section 1.

If we insert the results of the equations (15, 18) into equation (8) we have:

\[ u_{z_2} = (K_2 \cdot q_\perp^2 + K_3 \cdot q_\parallel^2) \left( \frac{\eta_{\text{twist}} \cdot \eta_3 \cdot q_\perp^2 + \eta_{\text{bend}} \cdot \eta_3 \cdot q_\parallel^2}{\eta_3 \cdot q_\perp^2 + \eta_3 \cdot q_\parallel^2} \right), \]

or equivalently:

\[ \frac{1}{2} \left( \frac{q_\parallel^2 + K_2 \cdot q_\parallel^2}{K_3 \cdot q_\parallel^2} \right) = B(q), \]

where \( B \) is defined as

\[ B(q) \equiv \frac{1}{K_3} \left\{ \frac{1}{2} (\eta_{\text{twist}} + \eta_{\text{bend}}) + \frac{1}{2} (\eta_{\text{twist}} - \eta_{\text{bend}}} \cdot z(q) \right\}. \]

with

\[ z(q) \equiv \left( \frac{\eta_3 \cdot q_\parallel^2}{\eta_1} - q_\perp^2 \right) \left( \frac{\eta_3 \cdot q_\perp^2 + q_\parallel^2}{\eta_1} \right). \]

Note that \( B \) is a linear function of \( z \). As will be described in section 3.2.1 the twist/bend elastic ratio can be obtained from measurements of the angular distribution of the scattered light in the same optical configuration. Because the components \( q_\perp \) and \( q_\parallel \) are known it is possible to evaluate the left-hand side of equation (30) using the measured line width. For \( z = 1 \) (\( q_\parallel = 0 \)) and \( z = -1 \) (\( q_\parallel = 0 \)), \( B \) does not depend on \( \eta_{3}/\eta_1 \) and is given by:

\[ B(q; q_\parallel = 0) = B_{z=-1} = \frac{\eta_{\text{twist}}}{K_3}, \]

\[ B(q; q_\perp = 0) = B_{z=1} = \frac{\eta_{\text{bend}}}{K_3}. \]

The ratio \( \eta_{3}/\eta_1 \) is most easily obtained from the slope of the function

\[ C(q) \equiv \frac{(B(q) - B_{z=-1})/(B(q) - B_{z=1})}{q_\parallel^2/\eta_1}, \]

plotted as a function of \( (q_\perp/q_\parallel)^2 \).

In practice scattering angles for which the conditions \( z = \pm 1 \) are fulfilled are not accessible. However, after plotting the experimental values of \( B \) versus \( z \) a linear curve is expected (cf. Eq. (31)). Hence by extrapolating one can obtain the viscoelastic ratios with the help of equations (33, 34). However this approach presumes knowledge of \( \eta_{3}/\eta_1 \) (cf. Eq. (32)). As this ratio is not known a priori we use a computer procedure to search for the value of \( \eta_{3}/\eta_1 \) that yields the best linear dependence of \( B \) on \( z \). An example of such a plot of \( B \) versus \( z \) is given in figure 9. According to equation (34) the value of the pure bend viscoelastic ratio is found at \( B_{z=-1} \). The pure twist viscoelastic ratio is derived from (cf. Eq. (33))

\[ \frac{\eta_{\text{twist}}}{K_3} = \frac{K_3}{K_2} \cdot B(z = 1). \]

Note that since \( \lim_{z \to -1} \left( \frac{K_3}{K_2} \cdot B \right) \) is independent of \( K_3/K_2 \), the value of \( K_3/K_2 \) is not directly involved in the determination of the twist viscoelastic ratio. Note also that the values of \( \eta_{\text{twist}}/K_3 \) obtained with this configuration can be compared with those from configuration \([I]\ [P] [F \perp] \) (cf. section 3.1).

Fig. 9. — A typical plot of \( B(z, u_z, K_3/K_2) \) versus \( z \) (\( q_\perp, q_\parallel/\eta_1 \)) after a fitting procedure where \( \eta_{3}/\eta_3 \) is found for which the data of \( B \) fit best a linear function of \( z \). The extrapolated values of \( B(1) = 2.50 \text{ ms}^{-2} \) and \( B(-1) = 0.503 \text{ ms}^{-2} \) correspond to the viscoelastic ratio \( \eta_{\text{twist}}/K_3 \) and \( \eta_{\text{bend}}/K_3 \) respectively.

Now that we know the values of \( B_{z=-1} \) and \( B_{z=1} \) we use equation (35) in order to determine \( \eta_{3}/\eta_1 \) more accurately from the slope of the curve through the points of \( C(q) \) versus \( (q_\parallel^2/q_\perp^2) \). An example of a plot of \( C(q) \) versus \( (q_\parallel^2/q_\perp^2) \) is shown in figure 10. We always found that the value of \( \eta_{3}/\eta_1 \) obtained from this slope was consistent with the value obtained by fitting \( B \).

3.2.1 Determination of the bend/twist elastic ratio. — With the help of configuration \([I\perp] [P \perp] [F \perp] \) the bend/twist elastic ratio \( K_3/K_2 \) can be obtained from measurements of the angular distribution of the scattered light.
Fig. 10. — A typical plot of $C(q)$ versus $(q_L/q_{11})^2$ (see Eq. (35)), which gives the viscosity ratio $\eta_1/\eta_3$. The full curve is the best fit through the points of a linear function, while the dashed line represents the best fit of a straight line through the origin.

As was pointed out in reference [2] the differential scattering cross section per solid angle is given by

$$\frac{d\sigma}{d\Omega} \sim \sum_{a=1,2} \left\{ G_a^2 \langle |\delta n_a(q)|^2 \rangle \right\}. \quad (37)$$

In contrast to the approach used for the determination of $K_1/K_2$ using configuration [I 1] [P 1] [F #1] (cf. Ref. [2]) it is not necessary here to take the effect of the finite sample size into account. It turned out that for samples with a thickness of 25 μm or more the neglect of finite size effects causes an error of less than 1% in $K_3/K_2$, which is smaller than the 2% experimental error in $K_3/K_2$.

As is explained in references [2, 9] the equipartition theorem may be applied in the derivation of the variance in equation (37). One obtains

$$\langle |\delta n_a(q)|^2 \rangle = \frac{k_B T}{V' K_a(q)}, \quad (38)$$

where $K_a(q)$ is defined in equation (6). The term $k_B$ is the Boltzmann constant, $T$ the absolute temperature and $V'$ the sample volume. Since for configuration [I]' [P] [F] $G_1 = 0$, the angle dependence of the scattering intensity $I(\theta)$ is given by:

$$I(\theta) \sim (K_2 q_{11}^2 + K_3 q_{11}^2)^{-1}. \quad (39)$$

Defining

$$J \equiv 1/(I(\theta) (q_{11}^2 + q_{11}^2)) \quad (40)$$

and

$$t \equiv (q_{11}^2 - q_{11}^2)/(q_{11}^2 + q_{11}^2), \quad (41)$$

equation (39) can be rewritten as:

$$J(t) = \text{const.} \left\{ \frac{1}{2} (K_3 + K_2) + \frac{1}{2} (K_3 - K_2) t \right\}, \quad (42)$$

which is linear in $t$. $J$ is obtained from a measurement of the angular distribution of the scattered light, $I(\theta)$, using equation (40). A typical example of a plot of $J$ versus $t$ is shown in figure 11.

Fig. 11. — Example of a plot of experimental values of $J$ versus $t$, as defined by equations (40, 41). The extrapolated values $J(+1) = 2.13$ and $J(-1) = 0.66$ give $J(+1)/J(-1) = 3.23$, which according to equation (43) should equal $K_3/K_2$.

From a linear fit through the datapoints of $J$ we can obtain $J(-1)$ and $J(+1)$ and thus we have

$$J(+1) = \frac{K_3}{K_2}. \quad (43)$$

3.3 SPLAY-BEND MIXTURES. — (cf. Table I with configurations [I] [P] [F] and [I] [H] [F]. For the configurations [I] [P] [F] and [I] [H] [F] (cf. Table I) $I_2 = 0$ and hence it is only the distortions due to the splay-bend mode which contribute to the spectrum ($\alpha = 1$). In this case we can use the same variable $x'$ defined in equation (27). Note that in the limiting case with $q_{11} = 0$, ($x' = 1$) now corresponds to pure splay. The calculated results for $x'$ as a function of $\theta$ are shown in figure 4 where we indicated the configurations [I] [P] [F] and [I] [H] [F] by E and D respectively. As figure 4 shows, the variable $x'$ varies by only a small amount over the
range of accessible scattering angles. In addition, the conditions 3) and 4) are not satisfied. Fortunately most of the information contained in the splay-bend spectrum could be measured using the splay-twist and bend-twist configurations [I \perp] [P \perp] [F \perp] and [I \|] [P \perp] [F \perp], described in sections 3.1 and 3.2.

In particular, we are now able to determine the splay/twist/bend elastic ratios, the splay, twist and bend viscoelastic ratios as well as the ratio of two Mićsowicz coefficients, $\frac{\eta_3}{\eta_1}$. As we have reported in reference [22], now that we have knowledge of the values of these ratios we are able to calculate the set of ratios of all Leslie coefficients, except $\alpha_1$. The only reason then for studying configurations [I \perp] [P \perp] [F \perp] and [I \|] [H \perp] [F \perp] would be to measure $\alpha_1 = \eta_{12}$, which occurs in equation (9) in the mixing term $(\eta_1 + \eta_2 + \eta_{12}) q^2_1 q^2_2$. In order to obtain $\eta_{12}$ from this mixing term with a fitting procedure one needs to study a range of scattering angles for which $q_1 \approx q_2$, i.e., in terms of equation (21), around $x' = 0$. Figure 12 shows that this condition holds for both configurations at a scattering angle of about 90°, which was unaccessible with the present experimental set-up. Moreover from literature [23, 15] one can expect $\eta_{12}$ to be very small compared to $\eta_1 + \eta_2$, $(\eta_{12}/(\eta_1 + \eta_2) \approx 0.04)$. Consequently even if the light scattering experiments were feasible any fitting procedure would inevitably yield highly inaccurate values for $\alpha_1$ because $\eta_{12}$ has to be obtained by subtracting $\eta_1$ and $\eta_2$ from the mixing term $(\eta_1 + \eta_2 + \eta_{12})$.

4. Results.

The techniques described in the previous sections were applied to determine the viscoelastic properties of APAPA as a function of temperature. APAPA (anisylidene-p-aminophenylacetate) has the following molecular structure:

\[
\begin{align*}
H_3C-O &-\longrightarrow C \quad H \\
& \quad \quad \quad \quad \quad \quad N \quad \quad \quad \quad \quad \quad O \\
& \quad \quad \quad \quad \quad \quad C \quad \quad \quad \quad \quad \quad CH_3
\end{align*}
\]

The molecules are fairly rigid and have a length of about 1.6 nm and a width of about 0.5 nm. APAPA is a nematic liquid crystal in the temperature range between $T_{KN} = 82°C$ and $T_{NI} = 109.0°C$ at a pressure of 1 atm. The subscripts stand for the crystalline state (K), for the nematic phase (N) and for the isotropic liquid state (I).

Fig. 12. — As an extension of figure 4, $x'$ (cf. Eq. (27)) is plotted versus the scattering angle for the configurations [I \perp] [H \perp] [F \perp] and [I \|] [H \perp] [F \perp] (case D) and configuration [I \|] [P \perp] [F \perp] (case E) for the entire range of scattering angles. See also table I.

Fig. 13. — The measured elastic distortion constant ratios $\frac{K_3}{K_2}$ (circles) and $\frac{K_3}{K_2}$ (dots) of APAPA as a function of the reduced temperature $T/T_{NI}$. The broken curves are fitted to Fréedericksz transition data of Leenhouts [5].

4.1 Elasticity. — Figure 13 shows the results of the splay/twist and the bend/twist elastic ratios, $\frac{K_1}{K_2}$ and $\frac{K_3}{K_2}$ respectively, as a function of the reduced temperature $T/T_{NI}$. The results have also been collected in table II. These ratios were determined from the angular distribution of the scattered light using the configuration [I \perp] [P \perp] [F \perp] and [I \|] [P \perp] [F \perp] respectively. A typical plot of an angular distribution is shown in figure 14. $G_1$, $G_2$, $q_1$ and $q_2$ were calculated with the refractive indices $n_\perp$ and $n_\|$, determined by Leenhouts [24].
Table II. — Experimental data for the distortion elastic-and viscoelastic ratios as a function of the reduced temperature, \( T/T_{NI} \) (\( T_{NI} = 109.2 \; ^\circ\text{C} \)).

1) Splay and twist distortion data obtained with configuration [I \( \perp \) ] [P \( \perp \) ] [F \( /\ell \) ]: \( K_1/K_2 \), \( \eta_{\text{splay}}/K_1 \) and \( \eta_{\text{twist}}/K_2 \).

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<td>0.9375</td>
<td>1.64</td>
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</table>

2) Twist and bend distortion data obtained with configuration [I \( \perp \) ] [P \( \perp \) ] [F \( /\ell \) ]: \( K_3/K_2 \), \( \eta_{\text{twist}}/K_2 \), \( \eta_{\text{bend}}/K_3 \) and \( \eta_3/\eta_1 \).

<table>
<thead>
<tr>
<th>( T/T_{NI} ) (( \pm ) 0.0001)</th>
<th>( K_3/K_2 ) (( \pm ) 2 %)</th>
<th>( \eta_{\text{twist}}/K_2 ) (( \times ) 10^9 ( \pm ) 2 % Pa.s/N)</th>
<th>( \eta_{\text{bend}}/K_3 )</th>
<th>( \eta_3/\eta_1 ) (( \pm ) 5 %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>---</td>
<td>2.00</td>
<td>4.48</td>
<td>0.599</td>
<td>0.28</td>
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<tr>
<td>0.9993</td>
<td>2.00</td>
<td>4.53</td>
<td>0.606</td>
<td>0.27</td>
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<td>4.75</td>
<td>0.603</td>
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<td>0.9980</td>
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<td>0.503</td>
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<td>4.61</td>
<td>0.482</td>
<td>0.24</td>
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<td>0.9926</td>
<td>2.56</td>
<td>5.15</td>
<td>0.490</td>
<td>0.23</td>
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<tr>
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<td>2.86</td>
<td>6.22</td>
<td>0.478</td>
<td>0.22</td>
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<td>0.9777</td>
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<td>6.44</td>
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<tr>
<td>0.9663</td>
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<td>0.9572</td>
<td>3.23</td>
<td>8.00</td>
<td>0.405</td>
<td>0.215</td>
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</table>

errors of 0.05 % in \( n_1 \) and of 0.5 % in \( \Delta n=n_1-n_2 \) cause an error of about 2 % in the elastic ratios.

Great care was taken to ensure that no pretransitional effects influenced the measurements at temperatures near the clearing temperature \( T_{NI} \). This is of importance since \( T_{NI} \) drops slowly with time (max. 0.05 \( ^\circ\text{C} \)/hour at \( T \ll T_{NI} \)), because thermal decomposition of the molecules decreases the purity of the nematic. The dashed lines in figure 13 represent best fits to data obtained by Leenhouts [5] from Freedericksz transitions.

4.2 Viscoelasticity. — From the determined band- widths as a function of scattering angle and using the measured elastic ratio data we determined the viscoelastic data of the splay, twist and bend distortions and the ratio of the Mięsowicz viscosities, \( \eta_1/\eta_3 \), in the way discussed in section 3. The results are given in table II. The data for the viscoelastic ratios are shown in figure 15, while \( \eta_3/\eta_1 \) is plotted in figure 16.

The results for the twist viscoelastic ratio obtained from different configurations agree within the experimental accuracy. For comparison we also show the results for the splay and twist viscoelastic ratios that would be obtained if one were to use the « single mode » method employed in reference [2]. With the latter method these ratios are obtained directly from the plot of \( \omega_m \) versus \( q_2^2 \). Of course this procedure is only expected to work if \( G_1 \ll G_2 \) (twist) or \( G_2 \ll G_1 \),
Fig. 14. — The measured angular intensity distribution
of APAPA at $T = 88^\circ$C, obtained with configuration $[I//][P//][F 1]$ (cf. Table I).

(splay) (e.g. cf. Fig. 4 of Ref. [2]). Obviously the twist
data thus obtained do not differ significantly from
the present results, but the splay data appear to be
systematically higher by some 10% over the entire
temperature range.

5. Discussion.

5.1 Elasticity. — Comparing our results for the
elastic ratios with those of Leenhouts [5] we observe
the same trends for both curves in figure 13. However,
our data for $K_1/K_2$ appear to be some 10%-20% larger than the data obtained from the Fréedericksz
transitions. Such a systematic difference has also
been observed before for several other compounds
e.g. Ref. [2]). In contrast, our data for $K_3/K_2$ fit the
data from the Fréedericksz transitions very well.
To our knowledge there is still no satisfactory expla-
nation for the observed systematic differences.

We can suggest two possible reasons for the observed
discrepancy:

a) Different anchoring conditions may have been
used in both experiments (although we have little
evidence [25, 26] to support this conjecture).

b) The elastic constants depend strongly on the
wave vector $q$ (which is about a factor 10-100 smaller
in the case of Fréedericksz transitions than in the
present experiments). This tentative explanation seems
even less likely.

5.2 Viscoelasticity. — From the measured splay
and twist viscoelastic ratios and the splay/twist
elastic ratio one can calculate the ratio of the splay/
twist viscosity coefficients, $n_{\text{tensile}}/n_{\text{twist}}$. In the same
way $n_{\text{bend}}/n_{\text{twist}}$ can be calculated. On the basis
of certain theoretical studies [15] it is reasonable

Fig. 15. — Experimental results of the determined splay
(squares, crosses), twist (dots, circles, plusses) and bend
triangles viscoelastic ratios versus the reduced tempe-
rate $T/T_{\text{ref}}$. The dots, circles, squares and triangles are
obtained with the help of computer fitting techniques.
The plusses and crosses are obtained using the technique
described in reference [2]. The dots, plusses, squares and
circles are from configuration $[I//][P//][F 1]$ while the
circles and triangles are from configuration $[I//][P//][F 1]$

Fig. 16. — Experimental results for the ratio of two Mie-
sowicz viscosities $\eta_1/\eta_1$, obtained by computer fitting
from configuration $[I//][P//][F 1]$.
Fig. 17. — The viscous ratios \( \eta_{\text{splay}} / \eta_{\text{twist}} \) (crosses, dots, triangles) and \( \eta_{\text{bend}} / \eta_{\text{twist}} \) (circles) versus the reduced temperature \( T/T_{NI} \). The dots and circles are calculated with viscoelastic ratios obtained with the help of computer fitting procedures, and using elastic ratios obtained from the angular intensity distributions of the scattered light. The crosses are obtained by using the viscoelastic ratios, determined according to the method of reference [2], whereas the triangles are obtained by using the elastic constants from the Frédéricz transitions [5].

We point out that a more detailed discussion in terms of molecular theories of viscoelastic properties of APAPA is presented in reference [22].

Acknowledgments.

We wish to thank Dr. W. H. de Jeu and Dr. F. Leenhouts for kindly supplying APAPA and for valuable and stimulating discussions. We are also grateful to Sheila McNab for making linguistic improvements and to Wendelies van der Meulen for typing the manuscript.

This work was performed as part of the research programme of the « Stichting voor Fundamenteel Onderzoek der Materie » (FOM) with financial support from the « Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek » (ZWO).

References

[8] MIĘSOWICZ, M., Bull. Intern. Acad. Polon. Ser. A (1936) 228; see also : MIĘSOWICZ, M., Nature 158 (1946) 27; note that \( \eta_1 \) and \( \eta_2 \) are interchanged.
[22] VANDER MEULEN, J. P., Ph. D. Thesis (Univ. of Utrecht) 1983, Chapter 4; see also VANDER MEULEN, J. P. and ZIJLSTRA, R. J. J., to be published.