PHYSICAL REVIEW A VOLUME 11, NUMBER 4 APRIL 1975

Quasielastic light scattering from nematic *p*-methoxybenzylidene-*p*′-*n*-butylaniline (MBBA)†

Hans Fellner,* Wilbur Franklin, and Stanley Christensen
Physics Department, Kent State University, Kent, Ohio 44242

(Received 19 August 1974)

The quasielastic scattering of laser light from nematic MBBA is studied utilizing homodyne procedures. The results stem from a comprehensive study of the half widths and areas of the "slow mode" peaks together with their temperature and angle dependence. The data taken at small angles yield the temperature-dependent ratios of the viscosity coefficients to curvature elastic constants for twist, bend, and splay. From these ratios, utilizing data of others, the temperature dependence of the twist elastic constant K_{22}, and twist, splay, and bend viscosity coefficients γ_1, η_s, and η_b, respectively, are determined. From the data taken at large angles the values of α_4' and α_v' (which is found to be negative) are determined at a reduced temperature, $T_R = 0.96$.

I. INTRODUCTION

The quasielastic scattering of laser light from nematic liquid crystals has been investigated in *p*-azoxyanisole (PAA) by the Orsay liquid crystal group[1] and in *p*-methoxybenzylidene-*p*′-*n*-butylaniline (MBBA) by Haller and Litster.[2,3] In this article we report new experimental observations on MBBA. The results stem from a comprehensive study of the areas and half widths of the "slow-mode" peaks together with their dependence on temperature and scattering angle. The following information concerning the material parameters of MBBA is obtained from the experimental results: (i) temperature and angle dependence of the ratios of viscosity to curvature elastic constants for twist, splay, and bend, (ii) the temperature dependence of the relative intensities, and, utilizing data from the literature, (iii) a determination of the twist elastic constant K_{22} and its temperature dependence, and (iv) evaluation of the η_s, η_b, α_v', α_4', and γ_1 viscosity coefficients and the temperature dependence of the first two coefficients. The results are consistent with the theory of light scattering given by the Orsay liquid crystal group[4] and by Martin, Parodi, and Pershan.[5] Effects of compressibility on mode 1[6,7] were not studied.

II. EXPERIMENTAL PROCEDURE

The experimental procedure was similar in style to that used previously[1-3] to study quasielastic scattering in nematic liquids. The spectrometer utilized was patterned after the one described by Ford and Benedek.[8] Data were taken by determination of the amplitude of the average photocurrent at various frequencies. The photocurrent amplitudes were then analyzed to obtain the half widths and areas of the broadened slow-mode peaks, which were Lorentzians.

A schematic of the homodyne spectrometer is shown in Fig. 1. A spectra Physics Model 125A He-Ne laser and a Coherent Radiation Model 54A argon-ion laser were used. Other than an initial exploratory study, most of the work was done with the Spectra Physics laser. To avoid problems encountered in sample heating the laser power was attenuated to less than 1 mW incident on the sample. The exposed sample area was approximately 1 mm^2. Single-beam, low-power laser polarizers of a modified Glan-Foucault type with an insertion loss of about 20% were used. The liquid-crystal samples were enclosed between 5×5 cm optical flats which were 6 mm thick. The flats were held apart by an 80 μm teflon spacer. The sample area was 9×15 mm. The sample holder was held rigidly in an Al chamber to minimize relative twisting of the flats which might result in optical activity. A thermally controlled chamber provided better than 0.1°C temperature stability. For certain geometrical arrangements a goniometer on a translation stage was utilized. The photomultiplier was an RCA-7265 (S-20 response) and its current was limited in use to less than 10^{-5} amp to insure linearity of response. A model 302A Hewlett Packard wave analyzer was used which had a frequency range of 20 Hz to 50 kHz and frequency and amplitude accuracies of ± 1% + 5 Hz and ± 5% of full scale, respectively.

The most suitable procedure for sample preparation was found to be the following. The optical flats were washed in detergent, rinsed in filtered running tap water for two hours, washed again in detergent and distilled water, dipped in several successive distilled water baths for a day and then dried and stored in an evacuated oven at 110°C. Homogeneous alignment was obtained with flats which were rubbed in one direction with 50–100 strokes of sterile gauze followed by checking of the sample alignment by rotating between crossed polarizers. Homeotropic alignment was obtained by the application of a 0.1% solution of lecithin in petroleum ether to the flats, drying for several hours, loading the sample, and then waiting for about 45 min for the sample to become uniformly dark between crossed polarizers. The liquid-crystal sample material was obtained from the Kent State University Chemistry Department and from the Varilight Corp. The nematic-isotropic transition temperature T_{NI} was checked and recorded regularly in the experimental runs.

The analysis of the photocurrent produced by the optical spectrum followed the development of Forrester[9] and of Cummins and Swinney.[10] Both heterodyning and homodyning procedures, which produced power spectra whose widths were equal to and twice that, respectively, of the optical spectrum were utilized. However, the preponderance of data reported here were obtained utilizing homodyning procedures. The power spectrum was obtained at different frequencies, the shot noise was subtracted, and the amplitude and inverse amplitude were plotted versus frequency. Fig. 2 gives typical data which are plotted using the power spectrum, which is given by

$$P(\omega) = \frac{\langle i \rangle^2 2\mu/\pi}{\omega^2 + 4u^2}, \qquad (1)$$

where u is the optical spectrum half width, ω is the circular frequency, and $\langle i \rangle$ is the average photocurrent.

III. RESULTS

The analysis of the results is based on the dispersion relations for the two types of slow modes given originally by the Orsay liquid crystal group.[4] Experimental conditions were chosen to fit limiting cases of these relations. The analysis of the experimental results utilized the index of refraction for MBBA.[11,12]

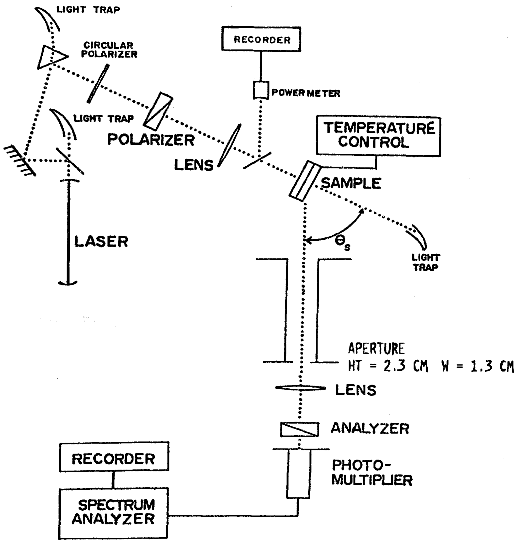

FIG. 1. Schematic of the homodyne spectrometer used for the quasielastic scattering studies on MBBA. The system is similar to that used by Ford and Benedek, Ref. 8.

Effects of compressibility do not affect mode 1. Therefore, since most of our results are for mode 1, the changes in the theory which are attributable to compressibility[6,7] do not alter the principal portion of our results. Another effect which is probably not a significant contributing factor in our light scattering results is the effect of density-director correlations.[7,13] The differential scattering cross section for light scattering from liquid crystals is proportional to self and cross correlations between density $\rho(\vec{q}, \omega)$ and the director $n(\vec{q}, \omega)$. The correlations which theoretically contribute[7,13] to the scattering are, in decreasing order of contribution, $\langle\langle n(\vec{q}, \omega) n(-\vec{q}, 0)\rangle\rangle$, $\langle\langle \rho(\vec{q}, \omega) n(-\vec{q}, 0)\rangle\rangle$, $\langle\langle n(\vec{q}, \omega) \rho(-\vec{q}, 0)\rangle\rangle$, and $\langle\langle \rho(\vec{q}, \omega) \rho(-\vec{q}, 0)\rangle\rangle$. If the incident and outgoing wavevectors are parallel, then all of the above correlations contribute to the scattering cross section; if they are perpendicular then only director-director correlations contribute. Theoretically it has been shown that the differential scattering cross section for density-director correlations is proportional to q^4 and director-director correlations proportional to q^2 in their lowest orders in q.[7] Consequently, in the hydrodynamic case, which applies to most light scattering configurations, scattering caused by density-director correlations (and the smaller director-density and density-density correlations) is negligible for small q.

Another possibility, which has not been investigated with respect to its applicability to light scattering, is the effects of molecular end chains

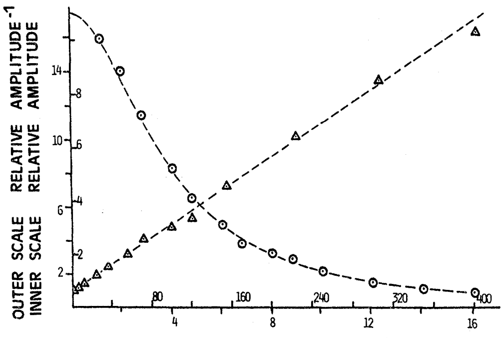

FIG. 2. Typical slow-mode dispersion data. The plot of relative amplitude vs frequency is a Lorentzian as shown by the circles; the plot of inverse relative amplitude versus frequency squared is essentially a straight line.

on slow mode scattering. Since one of the end chains in MBBA is considerably longer than in PAA the effects on light scattering may be affected, perhaps through short range order effects. This and other possible effects have not, however, been considered on a quantitative basis.

A. Ratios of viscosity coefficients to curvature elastic constants

The twist, splay, and bend viscosities stem from experimentally determined peak widths through the utilization of three limiting cases derived from Eqs. (IV.25a, b) of Ref. (4) when either $q_{\parallel} \ll q_{\perp}$ or $q_{\parallel} \gg q_{\perp}$. The ratio of the twist viscosity γ_1 to K_{22} versus the reduced temperature, $T_R = T/T_{NI}$, is presented in Fig. 3. In this case the data represent experimental runs at three different laboratory angles from 11.0° to 19.7° for which $q_{\parallel}^2 < 0.01 q_{\perp}^2$. Then, from Eq. (IV.25b) of Ref. (4), $\gamma_1/K_{22} = q_{\perp}^2/u_{S2}$. For angles larger than approximately 20° the contribution to u_{S2} from the $q_{\parallel}^2$ terms in Eq. (3) is greater than 1%.

Fig. (4) gives the temperature dependence of the ratio of the splay viscosity η_s to K_{11}. This case stems from the equation for u_{S1} when $\eta_s/K_{11} = q_{\perp}^2/u_{S1}$ (under the condition that $q_{\parallel}^2 \ll q_{\perp}^2$). The results which are shown include those for both the homeotropic and the homogeneous alignments.

For the bend modes Fig. (5) gives the ratio of the bend viscosity η_b to K_{33} vs T_R. This ratio is obtained when $q_{\perp}^2 \ll q_{\parallel}^2$; it stems from the case when $u_{S1} = u_{S2} = K_{33} q_{\parallel}^2/\eta_b$.

Representative values of the ratios of the twist, splay, and bend viscosities to their respective elastic constants for the selected reduced temperature of $T_R = 0.96$ are, in cgs units, given by $\gamma_1/K_{22} = 2.1 \times 10^6$, $\eta_s/K_{11} = 1.4 \times 10^6$ (homogeneous alignment) and $\eta_b/K_{33} = 2.8 \times 10^5$, respectively, with experimental uncertainties of ±7%.

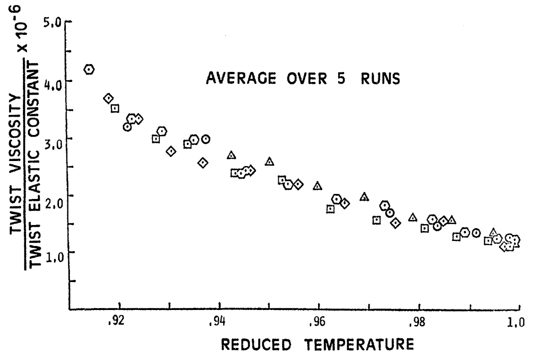

FIG. 3. The ratio of the twist viscosity γ_1 to the twist elastic constant K_{22} vs reduced temperature for mode 2.

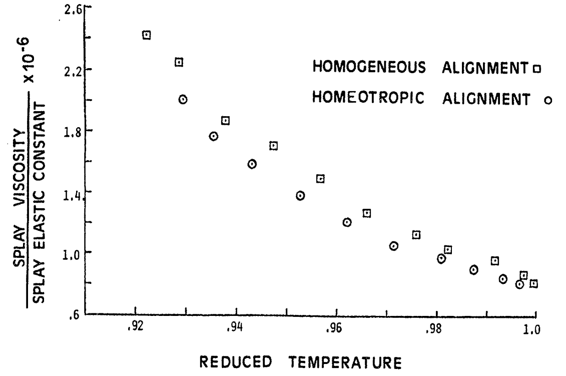

FIG. 4. The ratio of the splay viscosity η_s to the splay elastic constant K_{11} vs reduced temperature for mode 1.

B. Relative intensities

The line shapes were essentially Lorentzian and the relative intensities of scattered light, as determined by the areas, increased with T_R. For the twist mode the area increased linearly with temperature by approximately 13% for $0.92 \leq T_R \leq 1.0$ as shown by Fig. 6. For the splay mode the area increased by approximately 45% in the same range of T_R and was slightly greater than linear as shown by Fig. 7. The latter result was not consistent with the lowest order approximation which predicts that the scattering cross section is linear in temperature. The linear prediction follows from Lubensky's simplified equation[13] in which the differential scattering cross section is given by

$$\frac{d\sigma^2}{d\omega d\Omega} = k_B T \frac{\epsilon_a^2}{\lambda^4 K q^2}, \tag{2}$$

where ϵ_a, λ, and K are the dielectric anisotropy, wave length and an average elastic constant, respectively. Since ϵ_a and K are approximately

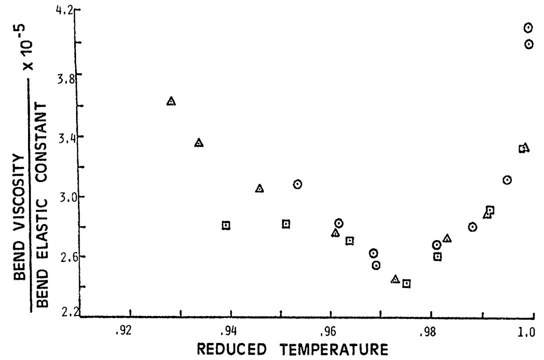

FIG. 5. The ratio of the bend viscosity η_b to the bend elastic constant K_{33} vs reduced temperature for mode 1, △, at a lab angle of 45.2° and mode 2, ○ and □, at lab angles of 37.7° and 43.5°, respectively.

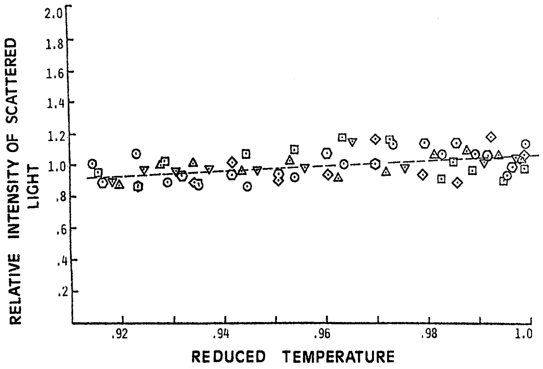

FIG. 6. Relative intensity of scattered light due to twist-order mode fluctuations vs reduced temperature for several experimental runs.

proportional to S (order parameter) and S^2, respectively,

$$\frac{d\sigma^2}{d\omega d\Omega} \propto \frac{k_B T}{\lambda^4 q^2}, \tag{3}$$

which shows a linear temperature dependence. (Much more rapid changes of area with temperature were observed with another member of and with mixtures from a homologous series which includes MBBA.)

C. Temperature dependence of K_{22}

From the twist data, which are shown in Fig. 3, the temperature dependence of the twist curvature elastic constant K_{22} is obtained utilizing the twist viscosity data of Meiboom and Hewitt[14] and Gasparoux and Prost.[15] The logarithmic plot of those authors' γ_1 data versus temperature is utilized together with the γ_1/K_{22} ratios of Fig. 3 to give K_{22} vs T_R, which is plotted in Fig. 8. Since the accuracy of the experimental technique used for the γ_1 determinations is approximately ±5%[16] and that of our measurements of the γ_1/K_{22} ratios is ±7%, the uncertainty of the K_{22} values is ±9%. This accuracy is an improvement over that of the direct measurements made by Haller[17] in which estimates of K_{22} were obtained with unknown uncertainties.

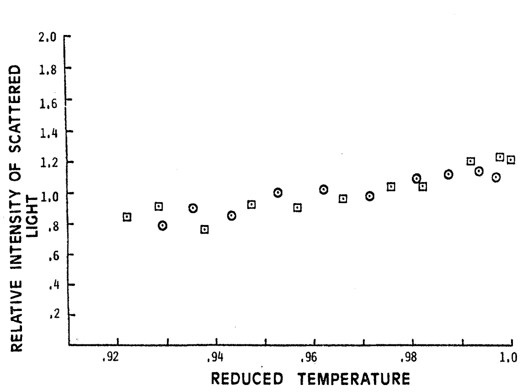

FIG. 7. Relative intensity of the light scattered by splay-order mode fluctuations in MBBA vs reduced temperature for homogeneous alignment □ and homeotropic alignment ○.

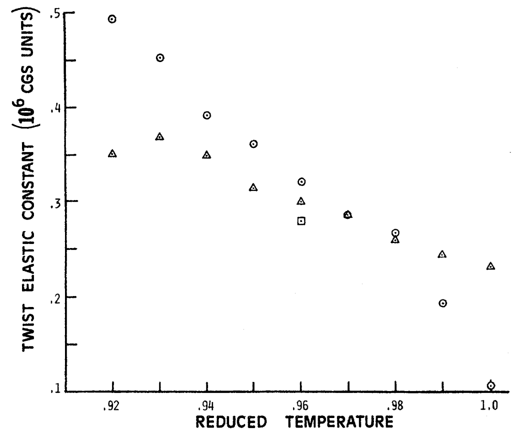

FIG. 8. Twist elastic constant K_{22} vs reduced temperature. K_{22} is obtained from Fig. 3 using γ_1 values from both Meiboom and Hewitt (Ref. 14) △ and Gasparoux and Prost (Ref. 15) ○. The values obtained by Williams and Cladis (Ref. 20) □ are shown for comparison.

D. Viscosity coefficients

Haller's values of K_{11} and K_{33} as a function of T_R are utilized together with the η_s/K_{11} and η_b/K_{33} ratios of Figs. 4 and 5, respectively, to obtain plots of η_s and η_b vs T_R. These plots are shown together in Fig. 9. The total uncertainty is approximately ±21% which stems from the following uncertainties added in quadrature: 20% for the elastic constants,[17] 7% for our half-width data, and 2% for the indices of refraction (which affect the values of $q_\perp$ and $q_\parallel$).

Also shown for comparison in Fig. 9 are the *splay* and *bend* viscosity coefficients determined by other experimenters as follows: (i) Haller,[17] who combined his K_{11} and K_{33} measurements[17] with earlier light scattering measurements by Haller and Litster[2,3] to obtain η_s and η_b (see squares in Fig. 9). Haller and Litster's measurements[2,3] allowed only the slopes, not the absolute values, of $\ln\eta$ vs T^{-1} to be determined. (ii) Gähwiller,[18] from capillary-flow viscosity data, as presented by Haller[17] (triangles in Fig. 9). (iii) Gasparoux and Prost,[15] who determined γ_1, which approximates η_s in MBBA,[17,18] from susceptibility measurements in rotating magnetic fields (circles in Fig. 9 show Haller's[17] interpretation of Gasparoux and Prost's[15] data). The dashed curve in Fig. 9 is

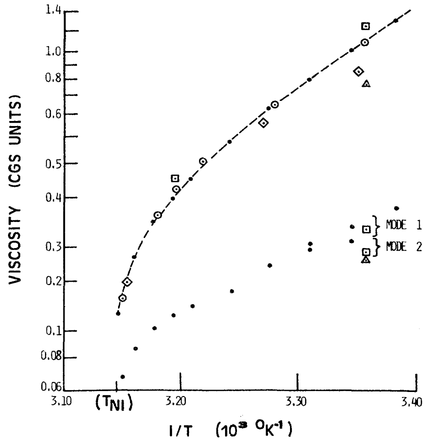

FIG. 9. Splay viscosity η_s (upper curve) and bend viscosity η_b (lower set of data) vs reduced temperature. These values are obtained from the data of Figs. 4 and 5 using K_{11} and K_{33} taken from Haller, Ref. 14. The values of η_s obtained by Haller (Ref. 17) □ and Gähwiller (Ref. 18) △ and the values of γ_1 obtained by Gasparoux and Prost (Ref. 15) ○ and Meiboom and Hewitt (Ref. 14) ◇ are shown for comparison. In order to compare the data of others taken with MBBA having different clearing points from ours, the data was normalized to a clearing point of 318 °K.

normalized to our average clearing point, $T_{NI} = 318\,^\circ$K. (iv) Meiboom and Hewitt,[14] who measured γ_1 using the method of susceptibility measurements in rotating magnetic fields (diamonds in Fig. 9). The lower set of data points in Fig. 9 is again normalized to $T_{NI} = 318\,^\circ$K. In the approximate temperature range given by $3.2\times10^{-3} \le 1/T \le 3.4\times10^{-3}$, η_s and η_b are found to have activation energies of 13.7 and 9.5 kcal/mole, respectively.

The values of the α_v' and α_4' coefficients are obtained from measurements at two different angles, θ_i and θ_j. From the Orsay theory[4]

$$\alpha_v' = \begin{vmatrix} N(\theta_i) & q_\perp^2(\theta_i) \\ N(\theta_j) & q_\perp^2(\theta_j) \end{vmatrix} \Bigg/ \begin{vmatrix} q_{\|}^2(\theta_i) & q_\perp^2(\theta_i) \\ q_{\|}^2(\theta_j) & q_\perp^2(\theta_j) \end{vmatrix} , \tag{4a}$$

$$\alpha_4' = \begin{vmatrix} q_{\|}^2(\theta_i) & N(\theta_i) \\ q_{\|}^2(\theta_j) & N(\theta_j) \end{vmatrix} \Bigg/ \begin{vmatrix} q_{\|}^2(\theta_i) & q_\perp^2(\theta_i) \\ q_{\|}^2(\theta_j) & q_\perp^2(\theta_j) \end{vmatrix} , \tag{4b}$$

where

$$N \equiv q_{\|}u_{S2}/(u_{S2}\gamma_1 - K_{22}q_\perp^2 - K_{33}q_{\|}^2) = q_{\|}^2\alpha_v' + q_\perp^2\alpha_4' . \tag{5}$$

The results, for $T_R = 0.96$, are given in Table I for three pairs of angles. The uncertainties for these values are ±21%. The averages of the three determinations of α_v' for different angular pairs[19] are $-0.43\,p^{-1}$ for $\gamma_1 = 0.60p$ and $-0.44p^{-1}$ for $\gamma_1 = 0.63p$. The large angular dependence of α_4' shown in Table I indicates that an average over these angular pairs is not meaningful and that the results depend on causes other than those considered by the Orsay Group. The reason for this disparity between the observations and the Orsay theory is unknown.

IV. DISCUSSION

In this section the results for the viscosity coefficients and elastic constants and their ratios for MBBA, which are obtained from the light-scattering data, are analyzed and discussed. The interesting effects of the Onsager reciprocity relations on the characterization of the viscosity parameters are pointed out.

The plots of K_{22} vs T_R shown in Fig. 8 give a comparison of our data for the K_{22}/γ_1 ratio analyzed utilizing two sets of data for γ_1 (those of Meiboom and Hewitt[14] and Gasparoux and Prost[15]) with the direct experimental determinations of K_{22} by Haller[17] and Williams and Cladis.[20] Our results for the two sets of γ_1 data are close to those of Haller (despite the experimental uncertainty of those measurements) for $0.94 < T_R < 0.99$ and differ significantly only for temperatures outside this range. If our results for the two sets of γ_1 data are averaged the temperature dependence of K_{22} is very close to that of S^2 for MBBA.[21] Since the relative intensity of scattered light from twist order mode fluctuations is linear in temperature (see Fig. 6) it is expected that the temperature dependence of K_{22} is close to that of S^2.

The agreement of our results (over the nematic temperature range) for the splay viscosity η_s (see Fig. 9) with those reported by Haller[17] (which were calculated from the light scattering results of Haller and Litster[2,3]) and with the γ_1

TABLE I. Values of the α_v' and α_4' viscosity coefficients in cgs units determined at $T_R = 0.96$ utilizing three different pairs of angles. The uncertainty of each of the reported values is ± 21%.

Angles used (in deg)	α_v' ($\gamma_1 = 0.60$)	α_v' ($\gamma_1 = 0.63$)	α_4' ($\gamma_1 = 0.60$)	α_4' ($\gamma_1 = 0.63$)
40.5 and 50.3	−0.47	−0.47	3.4×10^{-3}	3.4×10^{-3}
40.5 and 75.1	−0.42	−0.43	2.0×10^{-3}	2.1×10^{-3}
50.3 and 75.1	−0.40	−0.41	0.58×10^{-3}	0.59×10^{-3}

viscosity coefficient of Gasparoux and Prost[15] is very good. In addition, there is very little difference, especially at high temperatures, from the γ_1 data of Meiboom and Hewitt.[14] The value of η_s reported by Gähwiller[18] is the same as his value of γ_1 and this value, at $T_R = 0.94$, is 25% less than our value of η_s at that temperature. This is still reasonable agreement in the light of the differences in method and uncertainties in experimental data. For the bend viscosity, which is also shown in Fig. (9), the agreement between our results for mode 1 and that reported by Haller[17] at $T_R = 0.94$ is good—within 6%—while the mode-2 results are only about 11% apart. Gähwiller's[18] data (for an unknown mode) is again less than ours—22% less than the average of modes 1 and 2 and also less than Haller's.[17] However, again the agreement in magnitude is quite reasonable in the light of experimental differences and uncertainties. The γ_1 viscosity coefficient obtained from the γ_1/K_{22} ratio of Fig. (3) at $T_R = 0.94$ using Haller's[17] value of K_{22} is $0.75\,p$ and agrees very well with that obtained by Gähwiller[18] ($0.76\,p$) using the capillary-flow viscosity technique.

The calculation of the α_v' and α_4' coefficients, which was done using the γ_1 data of both Meiboom and Hewitt[14] and Gasparoux and Prost,[15] indicated a weak dependence on γ_1.

It is not possible to obtain viscosity coefficients from the light-scattering results in addition to those given already (such as the other constants obtained by the Orsay group[4]) for reasons which will be discussed now. Parodi[22] and Jähnig and Schmidt[6] showed that the Onsager reciprocity relations reduced the number of independent viscosity coefficients in incompressible nematic liquid crystals to five. When this reduction is taken into account the Orsay group's[4] equation for mode 1 contains four coefficients ($\gamma_1, \gamma_2, \beta$, and α_4 in Parodi's[22] notation) instead of five. Analytical solution of this equation, following the method used by the Orsay group,[4] for four different experimental configurations gives the nonphysical result that $\gamma_1 =$, $\gamma_2 = \beta$, and $\alpha_4 = 0$. Similarly, when Jähnig and Schmidt's equations for u_{S2}, which also utilize the Onsager relations, are solved simultaneously for different angles, another untenable result, $\gamma_1 = \gamma_2$, $\alpha_4 = \alpha_5 = 0$, is obtained. Therefore, the condition $\gamma_1 = -\lambda\gamma_2$, which was given initially by Ericksen[23] and Leslie[24] and discussed in detail by Martin, Parodi, and Pershan[5] must be utilized. When this is done it is not possible to evaluate λ from a set of simultaneous equations in γ_1, λ, β, and α_4, using the Orsay theory. Consequently, the results for mode 1 are limited to the evaluation of $\gamma_1, \eta_s, \eta_b, \alpha_4'$, and α_v' which has been done in the preceding sections. If λ and its temperature dependence are available from other experimental techniques then the remaining viscosity coefficients, together with their temperature dependences, can be obtained. However, experimental uncertainties in λ and the disparities between experimental techniques are magnified in the simultaneous solution of the modified Orsay equations for the viscosity coefficients.

---

*Presently with the Physics Department, Slippery Rock State College, Slippery Rock, Penn. 16057.

†Research supported, in part, by the Air Force Office of Scientific Research.

[1] Orsay Liquid Crystal Group, Phys. Rev. Lett. 22, 1361 (1969).

[2] I. Haller and D. Litster, Phys. Rev. Lett. 25, 1550 (1970).

[3] I. Haller and D. Litster, Mol. Cryst. Liq. Cryst. 12, 277 (1971).

[4] Groupe d'Etude des Cristaux Liquides (Orsay), Jour. Chem. Phys. 51, 816 (1969).

[5] P. Martin, O. Parodi, and P. Pershan, Phys. Rev. A 6, 2401 (1972).

[6] F. Jähnig and H. Schmidt, Ann. Phys. (N.Y.) 71, 129 (1972).

[7] S. Kess, dissertation (Kent State University, 1973).

[8] N. Ford and G. Benedek, Phys. Rev. Lett. 15, 649 (1965).

[9] A. Forrester, J. Opt. Soc. Am. 51, 253 (1961).

[10] H. Cummins and H. Swinney, Prog. in Optics 8, 135 (1962).

[11] M. Brunet-Geomain, C. R. Acad. Sci. Paris B 271, 1075 (1970).

[12] I. Haller, H. Huggins, and M. Freiser, Mol. Cryst. Liq. Cryst. 12, 277 (1971).

[13] T. C. Lubensky, Phys. Rev. A 2, 2497 (1970).

[14] S. Meiboom and R. C. Hewitt, Phys. Rev. Lett. 30, 261 (1973).

[15] H. Gasparoux and J. Prost, J. Phys. (Paris) 32, 953 (1971).

[16] Estimated from the reproducibility of γ, reported in Refs. 12 and 16.

[17] I. Haller, J. Chem. Phys. 57, 1400 (1972).

[18] Ch. Gähwiller, Phys. Lett. 36A, 311 (1971).

[19] H. Fellner, W. Franklin, and S. Christensen, Bull. Am. Phys. Soc. 18, 658 (1973). Note misprint in which α_v' was reported as $-0.34\,p^{-1}$ instead of $-0.43\,p^{-1}$.

[20] C. Williams and P. Cladis, So. State Commun. 10, 357 (1972).

[21] S. Jen, N. A. Clark, P. S. Pershan, and E. B. Priestly, Phys. Rev. Lett. 31, 1552 (1973).

[22] O. Parodi, J. Phys. (Paris) 31, 581 (1970).

[23] J. Ericksen, Arch. Ratl. Mech. Anal. 4, 231 (1960).

[24] F. Leslie, Quart. J. Mech. Appl. Math. 19, 356 (1966); Arch. Ratl. Mech. Anal. 28, 265 (1968).