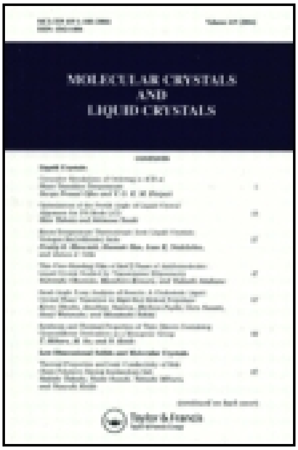

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A Light-Scattering Study of Pretransitional Behavior Around the Isotropic-Nematic Phase Transition in Alkylcyanobiphenyls

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A Light-Scattering Study of Pretransitional Behavior Around the Isotropic-Nematic Phase Transition in Alkylcyanobiphenyls†

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Light-scattering measurements have been performed on the homologous series of P,P'-alkylcyanobiphenyls in a temperature range of about 10°C above the clearing temperature. In a temperature range of a few degrees above the phase transition deviations were observed from the $(T - T_c^*)^{-1}$ dependence expected from the Landau-de Gennes theory. These deviations are rather similar for nematic-isotropic and smectic-isotropic transitions. Due to the high scattering intensity multiple scattering occurs for the lower homologues. This is demonstrated by experiments where multiple scattering is enhanced by reducing the wavelength of the incoming beam. It is shown that any dependence of the depolarization ratio on the temperature is a sensitive criterion for multiple scattering. The observed deviations from a $(T - T_c^*)^{-1}$ dependence can be accounted for by including non-Gaussian terms in the Landau free energy, provided the inverse of the momentum cut-off is taken to be of the order of the length of the molecule.

I. INTRODUCTION

Light scattering is a well known and useful tool for studies of pretransitional effects near phase transitions of fluids. In the case of the smectic- or nematic-isotropic phase transition the light scattering in

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the isotropic phase is mainly due to the orientational fluctuations of the anisotropic molecules. When approaching the phase transition temperature T_c the intensity of the scattered light increases strongly due to the increased correlation between the fluctuations about the order parameter tensor, which has an average value zero in the isotropic phase. This pretransitional behaviour is usually described in terms of the Landau-de Gennes theory.[1] However, since the very first measurements,[2] it has been recognized that close to T_c the light scattering deviates from the mean field behaviour predicted theoretically. Though several authors have studied this point again, both by light-scattering[3,4] and by other techniques,[5-8] the origin of these deviations is not clear yet. In fact there is even some controversy about the correct experimental characterisation of these deviations. In this context we note that in the case of fluids it is well known that close to the critical point the turbidity of the fluid becomes so large that part of the incident light is scattered more than once before reaching the detector. This multiply scattered light changes the depolarisation ratio of the detected signals. Though in liquid crystals due to the first order character of the phase transition the critical point T_c^* lies below the temperature T_c where the actual transition takes place, the scattering intensity can be quite large in the isotropic phase, and as will be shown multiple scattering can occur.

It is the purpose of this paper to study in some detail the pretransitional light scattering in the isotropic phase of the *P*,*P'*-alkylcyanobiphenyls, to be denoted by *nCB*, where *n* is the number of carbon atoms in the alkyl chain. Up to $n = 9$ T_c refers to the transition nematic-isotropic, from $n = 10$ on, to a transition smectic A-isotropic. Two series of experiments have been carried out. The full series for $n = 5-12$ has been studied at a wavelength $\lambda = 633$ *nm*. To take advantage of the proportionality between the scattered intensity and λ^{-4}, in addition 6CB, 8CB and 10CB were studied at 488 *nm*. The results will be compared with the Landau-de Gennes theory, which will be taken beyond the Gaussian approximation. In principle the deviations of the inverse scattered intensity from a linear dependence on T can be accounted for by incorporating higher order terms in the free energy, provided the required cut-off is associated with the dimension of a short-range ordered group of several molecules.

The plan of the paper is as follows. In the next section first the theoretical formulas are summarized, both for the extended Landau-de Gennes theory, and for the description of multiple scattering. In Section *III* the experimental set-up is described. Section *IV* gives the results and Section *V* a concluding discussion.

II. THEORETICAL

A. Theory of the nematic-isotropic phase transition

The natural order parameter characterising a uniaxial nematic phase is a symmetric traceless second-rank tensor **Q** with elements

$$Q_{\alpha\beta} = \langle \hat{\nu}_\alpha \hat{\nu}_\beta \rangle - \frac{1}{3}\delta_{\alpha\beta}, \qquad \text{where} \tag{1}$$

$\hat{\nu}$ is the unit vector giving the direction of the unique molecular axis. The brackets denote an ensemble average over all orientations. In the Landau-theory the free energy density of the nematic phase is expanded in terms of **Q** as[1,9]

$$F = F_0 + \frac{1}{2} A \, Tr\, \mathbf{Q}^2 + \frac{1}{3} B \, Tr\, \mathbf{Q}^3 + \frac{1}{4} C (Tr\, \mathbf{Q}^2)^2$$

$$+ \frac{1}{2} L_1 (\partial_\alpha Q_{\beta\gamma})^2 + \frac{1}{2} L_2 (\partial_\beta Q_{\beta\gamma})^2. \tag{2}$$

Here F_0 is the free energy density of the isotropic phase, and $A = a(T - T_c^*)$ determines the phase transition. The general expansion is kept to the fourth order, while only the lowest order space derivative invariants of **Q** have been retained. The coefficients L_1 and L_2 are related to the elastic constants K_1, K_2 and K_3 in the nematic phase, ∂_α indicates derivatives with respect to the space coordinates, and a summation over repeated indices is implied.

To describe light scattering in the isotropic phase, in the Gaussian approximation cubic and higher order terms in Eq. (2) are disregarded. In addition we shall take for simplicity $L_2 = 0$ and replace L_1 by the average value $\bar{L}$. Fourier-analysing the free energy in terms of the scattering wave vectors $\tilde{\mathbf{q}}$ one finds

$$F = F_0 + \frac{1}{2} \sum_q (A + \bar{L} q^2) |Q_{\alpha\beta}(\mathbf{q})|^2. \tag{3}$$

Applying the equipartition theorem $\langle |Q_{\alpha\beta}|^2 \rangle$ can be calculated. If the incident light is polarised along the z-axis, the depolarised component of the scattered light is proportional to the differential scattering cross-section $\sigma_\perp$

$$I_\perp \sim \sigma_\perp = (\Delta\epsilon_m^2/\lambda^4) \langle |Q_{yz}(\mathbf{q})|^2 \rangle = \frac{1}{2} (\Delta\epsilon_m^2/\lambda^4) G_0(\mathbf{q}). \tag{4a}$$

Here $\Delta\epsilon_m$ is the maximum optical dielectric anisotropy as would be observed for a fully aligned system. Furthermore

$$G_0(\mathbf{q}) = \frac{k_BT}{A + \overline{L}q^2} = \frac{k_BT}{a(T - T_c^*)(1 + \xi_0^2q^2)}, \tag{4b}$$

where $\xi_0 = (\overline{L}/A)^{1/2}$ is the correlation length. Similarly

$$I_\| \sim \sigma_\| = (\Delta\epsilon_m^2/\lambda^4)\,\langle|Q_{zz}(\mathbf{q})|^2\rangle = \frac{2}{3}\,(\Delta\epsilon_m^2/\lambda^4)G_0(\mathbf{q}). \tag{4c}$$

Due to the first-order nature of the transition one cannot approach T_c^* very closely, and therefore $\xi^2q^2 << 1$.

Hence one can write

$$I^{-1}T \sim a(T - T_c^*). \tag{5}$$

Furthermore one finds quite generally $I_\|/I_\perp = 4/3$.

To calculate the contributions of the third and fourth order terms in Equation (2) to the correlation function $G(q)$, one can use perturbation theory with the Gaussian model as the zeroth order approximation.[9–11] According to Gramsbergen *et al.*[11] the result is to replace $G_0(\mathbf{q})$ by $G(\mathbf{q})$ given by

$$G^{-1}(\mathbf{q}) = \frac{A}{k_BT} + \frac{C}{\overline{L}\xi_0}f_C - \frac{B^2\xi_0}{\overline{L}^2}f_B + q^2\left[\frac{\overline{L}}{k_BT} + \frac{B^2\xi_0^3}{\overline{L}^2}g_B\right], \tag{6}$$

with

$$f_C = (7/2\pi^2)(\phi - \tan^{-1}\phi),$$

$$f_B = \frac{7}{24\pi^2}\left(\tan^{-1}\phi - \frac{\phi}{1 + \phi^2}\right)$$

$$g_B = \frac{7}{96\pi^2}\left[\tan^{-1}\phi + \frac{\phi(\phi^2 - 1)}{(1 + \phi^2)^2}\right],$$

and finally

$$\phi = \xi_0 q_m.$$

Here q_m is the maximum wave vector over which the integration in

q-space is to be taken. In the case of solid state physics this is at the first Brillouin zone. In our situation one can use an "amorphous" analogue the Debye sphere, with

$$q_m = (6\pi^2\rho)^{1/3}, \tag{7}$$

where ρ is the particle density.

B. Theory of double scattering

Schroeter *et al.*[12] used the theory of Reith and Swinney[13] and Oxtoby and Gelbart[14] to analyse the multiple scattering contribution to the scattered light in the binary liquid mixture methanol-cyclohexane. Following their approach we consider an incident plane polarized light beam scattered on a collection of single scatterers in a volume V_1, and write for the differential scattering cross-section

$$\sigma(\hat{\mathbf{e}}_i,\mathbf{k}_i,\mathbf{k}_1) = \sigma_0 f \sin^2(\hat{\mathbf{e}}_i,\hat{\mathbf{k}}_1), \tag{8}$$

$\mathbf{k}_i$ is the wave vector of the incident plane wave,
$\hat{\mathbf{e}}_i$ is a unit vector giving the polarization of this wave,
$\mathbf{k}_1$ is the scattered wave vector at position $\mathbf{r}_1,\hat{\mathbf{k}}_1, = \mathbf{k}_1/|\mathbf{k}_1|$,
$|\mathbf{q}| = |\mathbf{k}_i - \mathbf{k}_1| = (4\pi n/\lambda)\sin(\theta/2)$, where n is the refractive index and θ the scattering angle.
Finally $f = (1 + \xi^2 q^2)^{-1}$ is the correlation factor that appears in Equation (4b). As already noted in practice $f \simeq 1$.

The scattered wave $\mathbf{k}_1$ of polarisation $\hat{\mathbf{e}}_1$ illuminates a collection of double scatterers in volume V_2. Let the position of the double scatterer be $\mathbf{r}_2$. If light is detected at $\mathbf{r}_3$ in a direction perpendicular to the incident wave ($\theta = 90°$) and $r_3 >> r_1, r_2$, then according to reference 12 one can write for the double scattered intensity in a point at the detector surface

$$I_{p,\perp} = \frac{\sigma_p^2}{r_3^2}\int_{V_1}\int_{V_2} I_i(\mathbf{r}_1)\,\frac{x_{2,1}^2 z_{2,1}^2}{r_{2,1}^6}\,\mathrm{d}V_1\mathrm{d}V_2, \qquad p = \|,\perp, \tag{9a}$$

$$I_{p,\|} = \frac{\sigma_p^2}{r_3^2}\int_{V_1}\int_{V_2} I_i(\mathbf{r}_1)\,\frac{(x_{2,1}^2 + y_{2,1}^2)^2}{r_{2,1}^6}\,\mathrm{d}V_1\mathrm{d}V_2, \qquad p = \|,\perp, \tag{9b}$$

where $\mathbf{r}_{2,1} = |\mathbf{r}_1 - \mathbf{r}_2|$ and $\mathbf{r}_{2,1} = x_{2,1}\hat{\mathbf{x}} + y_{2,1}\hat{\mathbf{y}} + z_{2,1}\hat{\mathbf{z}}$.
The turbidity τ is defined by

$$I = I_0 \exp(-2\tau\,\Delta y), \tag{10}$$

where Δy is the distance the incoming beam has travelled through the sample, and I_0 is the intensity at the entrance of the cell. The total polarized and depolarized intensities are now:

$$I_{\parallel} = \alpha \exp(-2\tau\Delta y)\, \sigma_{\parallel} + \beta\sigma_{\parallel}^2 + \gamma\sigma_{\perp}^2, \tag{11a}$$

$$I_{\perp} = \alpha \exp(-2\tau\Delta y)\, \sigma_{\perp} + \beta\sigma_{\perp}^2 + \gamma\sigma_{\parallel}^2, \tag{11b}$$

with

$$\alpha = \int_{V_1 \cap V_D} I_i(\mathbf{r}_1)/r_3^2 \, dV,$$

$$\beta = \int_{V_1}\int_{V_2} I_i(\mathbf{r}_1)(x_{2,1}^2 + y_{2,1}^2)^2/r_{2,1}^6 \, dV_1 dV_2,$$

$$\gamma = \int_{V_1}\int_{V_2} I_i(\mathbf{r}_1)x_{2,1}^2 z_{2,1}^2/r_{2,1}^6 \, dV_1 dV_2,$$

The measured scattering intensity is obtained by integrating over the apertures A_1 and A_2. V_D is the volume in the scattering cell seen by the detector (see Figure 1); V_2 is the liquid volume in the cell. Neglecting turbidity corrections the depolarization ratio is

$$\frac{I_{\parallel}}{I_{\perp}} = \frac{\frac{4}{3} + \frac{4}{3}\frac{\beta}{\alpha}\sigma_{\parallel} + \frac{3}{4}\frac{\gamma}{\alpha}\sigma_{\parallel}}{1 + \frac{3}{4}\frac{\beta}{\alpha}\sigma_{\parallel} + \frac{4}{3}\frac{\gamma}{\alpha}\sigma_{\parallel}}. \tag{12}$$

III. EXPERIMENTAL

The intensity of the scattered light was measured at an angle of 90° with respect to a vertically polarized laser beam (see Figure 1). Both the polarized and the depolarized components were determined. The output signal from the photomultiplier was fed into a lock-in amplifier, using a reference signal obtained from a chopper in the incident beam. The incoming intensity of the laser beam as well as the transmitted intensity through the cell were detected by a photo diode. The sample cell was placed in a two-stage oven, the inner part of which

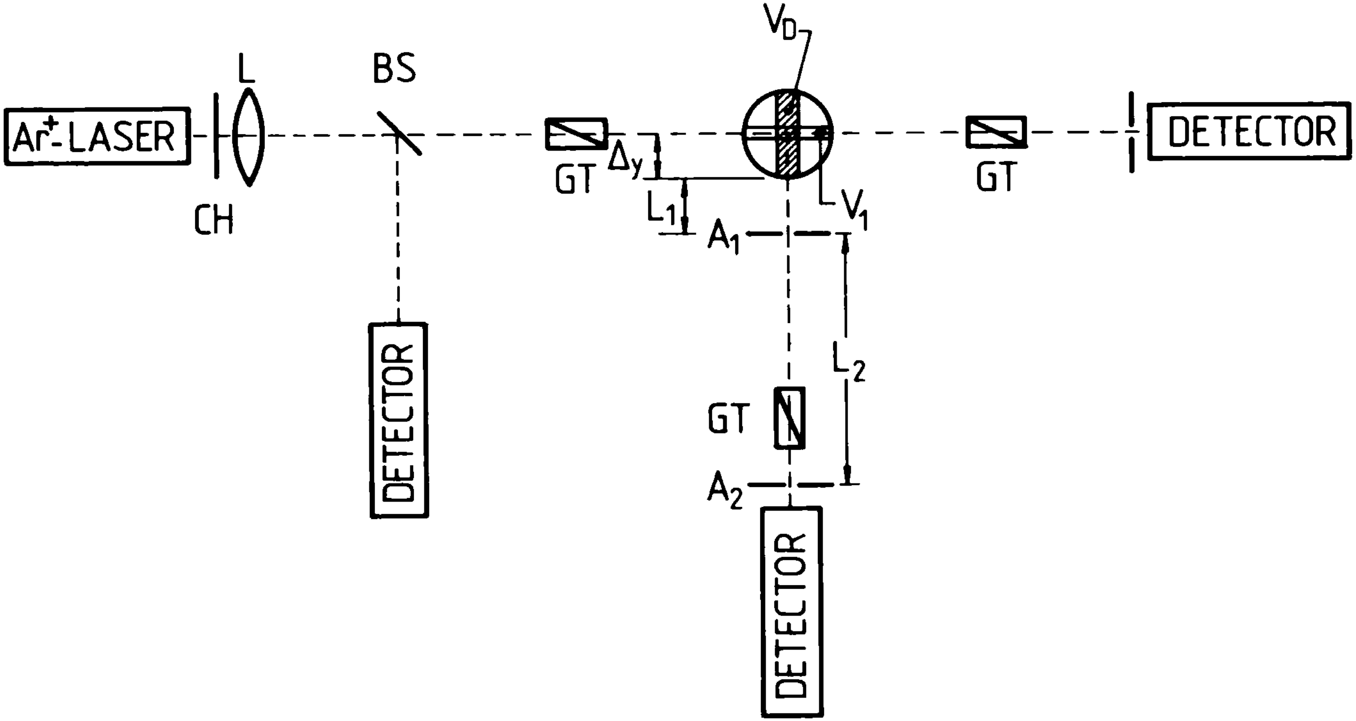

FIGURE 1 Schematic drawing of the experimental set-up; BS: beam-splitter; GT: Glan-Thompson prism polariser.

is a copper block, temperature regulated to within 1 mK. The temperature was measured by means of a HP quartz thermometer, with a resolution better than 1 mK.

Two types of sample cells were used in connection with different lasers. A He-Ne laser (λ = 633 nm) was used in combination with a rectangular scattering cell with an optical path length of 10 mm. The diameter of pinhole A_1 was 0.1 mm, while L_1 = 140 mm. In this way the nCB series was measured with n = 5–12. More accurate measurements to determine the possible influence of double scattering were carried out for 6CB, 8CB and 10CB only. An Ar^+ laser (λ = 488 nm) was used in combination with a cylindrical scattering cell (ϕ = 13 mm). The aperture A_1 was varied between 0.2 and 3 mm, while A_2 = 1 mm, L_1 = 110 mm, and L_2 = 530 mm.

The liquid crystalline compounds were obtained from BDH (Poole, Dorset, U.K.) and used without further purification. The clearing temperatures are given in Table I. Note that from n = 10 this refers to a transition smectic A-isotropic, in contrast to earlier reports that give for 11CB a small nematic range. The disappearance of this nematic phase is attributed to the greater purity of the present batches.[15]

IV. RESULTS

We shall start with results for the scattering intensity for the full nCB series at long wavelength (λ = 633 nm). In Figure 2 a typical curve is given for 8CB. In Figure 3 the results are plotted as $I_G/I_{\parallel}$ thus emphasizing the deviations from the straight line predicted by the Gaussian approximation (G) of the mean-field theory. For the sake of clarity each curve is shifted with respect to the previous one by a

TABLE I

Clearing temperatures T_c of the nCB series and critical temperatures T_c^* as obtained from a linear least-square fit of $T/I(T)$

n	T_c/°C	T_c^*/°C	$T_c - T_c^*$/°C
5	34.70 ± 0.05	33.3 ± 0.1	1.4
6	29.27	27.9	1.4
7	42.65	41.4	1.3
8	40.42	39.4	1.0
9	49.70	48.2	1.5
10	50.85	46.6	4.2
11	56.90	51.6	5.3
12	58.05	50.4	7.7

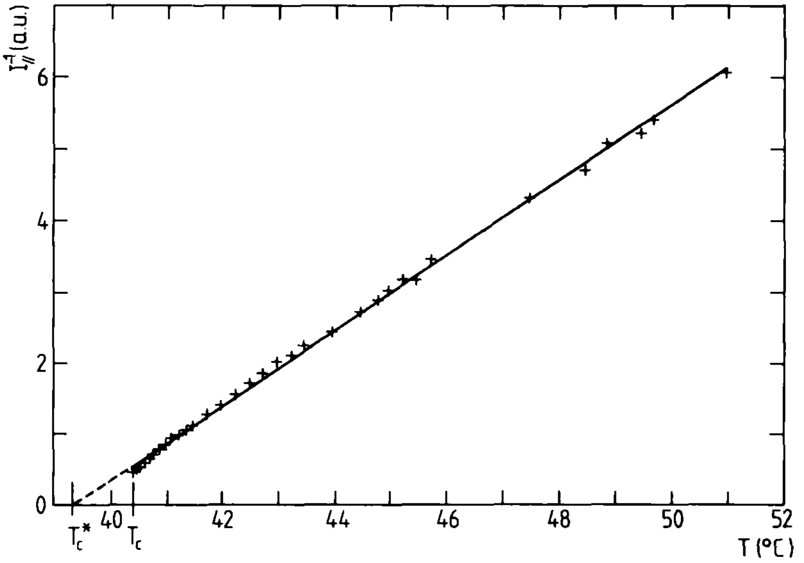

FIGURE 2 Inverse scattering for 8CB at 633 nm. Full line gives the best fit to all data points for a straight line.

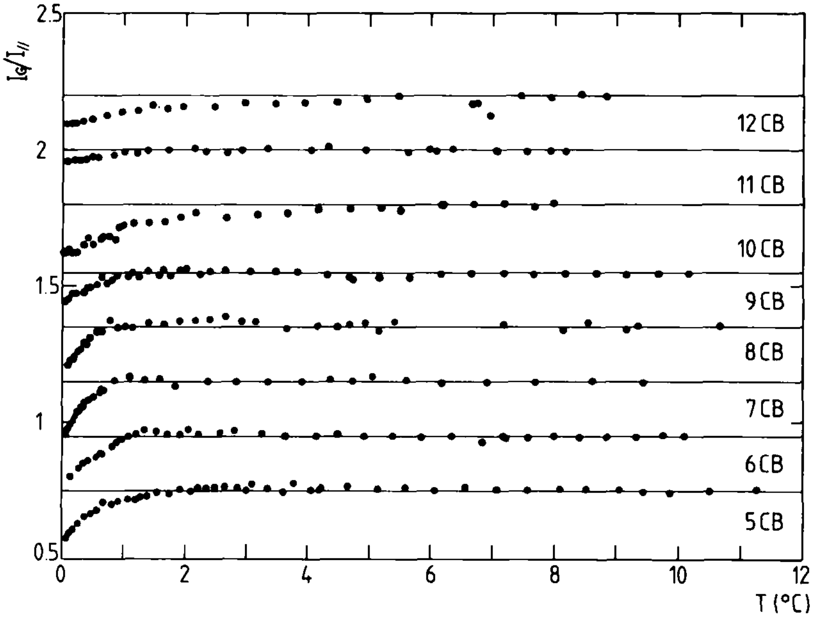

FIGURE 3 Light scattering results for the nCB series at 633 nm, relative to I_G. I_G (G for Gaussian approximation) is determined from the best straight line for data points away from T_c.

certain amount. The values for T_c^* obtained from the Gaussian approximation are given in Table I.

To study the influence of multiple scattering on the deviations from $(T - T_c^*)^{-1}$ behaviour, the Ar$^+$ laser (λ = 488 nm) was used. The polarized and depolarized scattering intensities for 6CB, 8CB and 10CB were measured for various values of the aperture diameter A_1. In Figure 4 the results are shown for 6CB at two temperatures. The intensities are normalized with regard to the smallest aperture. The stronger increase of the intensity for $A_1 > 1$ mm at the lowest temperature indicates the presence of multiple scattering. This is once more illustrated in Figure 5, where the ratio of the intensities at apertures of 3 and 1 mm is plotted for 6CB, 8CB and 10CB. For 8CB and 10CB this ratio is constant within the experimental accuracy.

According to Equation (12) the influence of multiple scattering should also be seen in the depolarization ratio $I_\parallel/I_\perp$. These results are plotted for all three components in Figure 6a for A_1 = 3 mm and in Figure 6b for A_1 = 1 mm. The ratio $I_\parallel/I_\perp$ decreases on approaching T_c, which effect depends on the value of $T_c - T_c^*$.

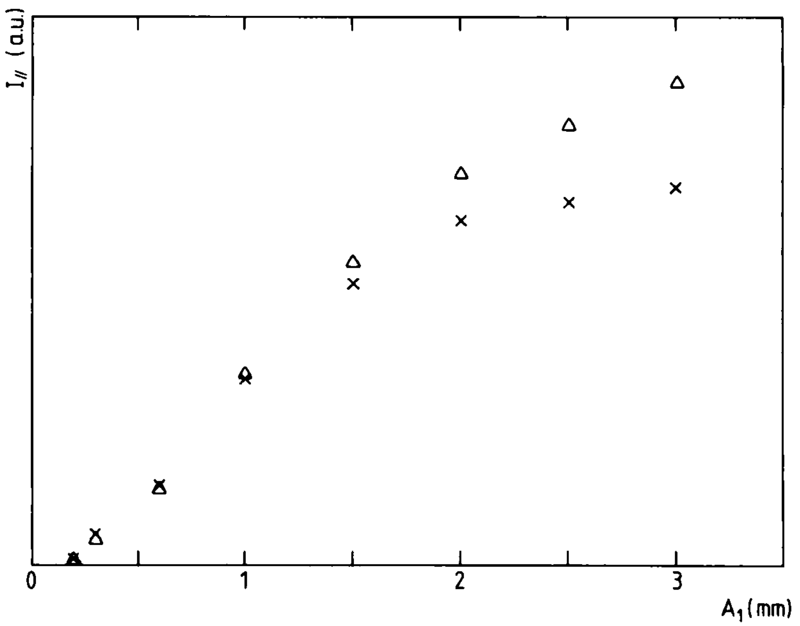

FIGURE 4 Polarized light scattering of 6CB at 488 nm as a function of the aperture A_1; ×: 38.27°C, Δ: 29.19°C.

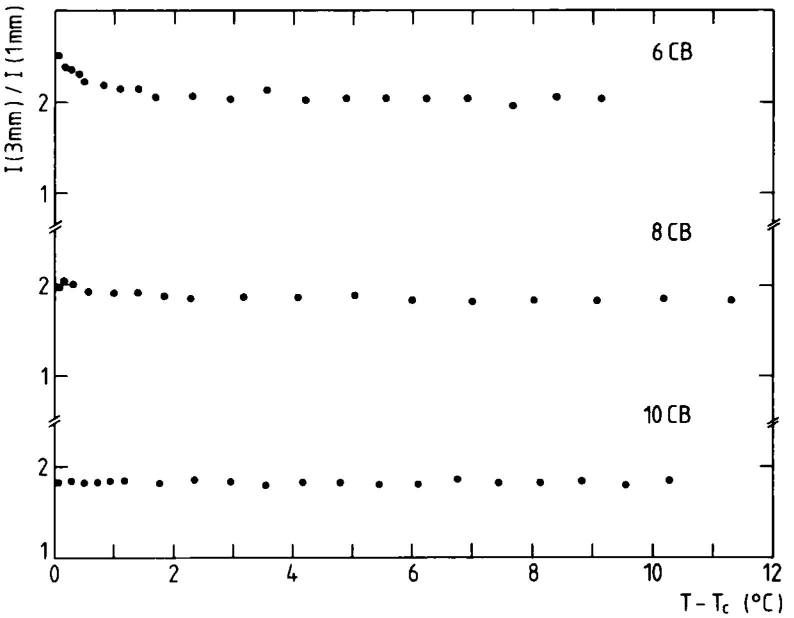

FIGURE 5 Ratio $I(3\text{ mm})/I(1\text{ mm})$ for 6CB, 8CB and 10CB where the index refers to the aperture diameter A_1.

Finally the influence of the turbidity on the scattered intensity has been considered by measuring the transmitted intensity through the cell. This is found to be a minor effect as only at a few points close to T_c can some influence be seen.

V. DISCUSSION

A. Influence of multiple scattering

From Figure 4 it is clear that for $A_1 \leqslant 1$ mm the multiple scattering contribution is not noticeable in the aperture dependence of the scattered intensity. This is approximately the size of the laser beam in the scattering cell. We therefore plotted in Figure 5 the ratios of the intensities for $A_1 = 3$ mm and $A_1 = 1$ mm for 6CB, 8CB and 10CB. For 10CB there is no dependence in temperature, for 8CB only for the last three points close to T_c, so that here also double scattering can be disregarded.

The depolarization ratio $I_{\parallel}/I_{\perp}$ turned out to be the best criterion to check for double scattering. The results of Figure 6 can be described by a function:

$$\frac{I_{\parallel}}{I_{\perp}} = \frac{\frac{4}{3} + \frac{3}{4}\frac{PT}{(T - T_c^*)}}{1 + \frac{4}{3}\frac{PT}{(T - T_c^*)}} + Q, \tag{13}$$

where P and Q are adjustable parameters. This function can be derived from Equation (12) under the assumption $\beta/\alpha << \gamma/\alpha$. This means that the polarized double scattering is much smaller than the depolarized double scattering. Neglecting the term in β/α one finds

$$P = \frac{\gamma}{\alpha}\frac{2}{3}\frac{\Delta\epsilon_m^2 k_B T}{a\lambda^4}, \tag{14}$$

while Q is a background term. Determination of P for 6CB leads to the ratio $P(3\text{ mm})/P(1\text{ mm}) = 2$. Because this is a geometrical factor we can apply it also to 8CB and 10CB, using the proportionality between P and $\Delta\epsilon_m^2/a$. Coles and Strazielle[3b] tabulated the values of $\Delta\epsilon_m^2$ while a is a constant from the Landau free energy. Using these data P can be calculated for 8CB and 10CB. The curves for $I_{\parallel}/I_{\perp}$ obtained in this way are shown in Figure 6 and describe the experiments very well.

The influence of double scattering can be reduced by decreasing σ, because the double scattering is proportional to σ^2, and by reducing V_1, V_2 and V_D. A reduction of σ has been accomplished in the measurements given in Figure 3 by increasing the wavelength λ. As these measurements are somewhat less precise it is not possible to determine a value for the coefficient P. Nevertheless comparing the various results, and especially looking at the deviations of $I_{\parallel}/I_{\perp}$ from 4/3, it is clear that multiple scattering can be disregarded for 7CB and higher homologues.

B. Characterization of the phase transition

The experimental results for the scattering in the isotropic phase of the nCB series (Figures 2–3) lead to two conclusions that should be made explicit:

(i) For all alkyl chain length n the experimental points bend downwards from the G-line when approaching the phase transition. There is no indication of a reversal of this trend very close to T_c

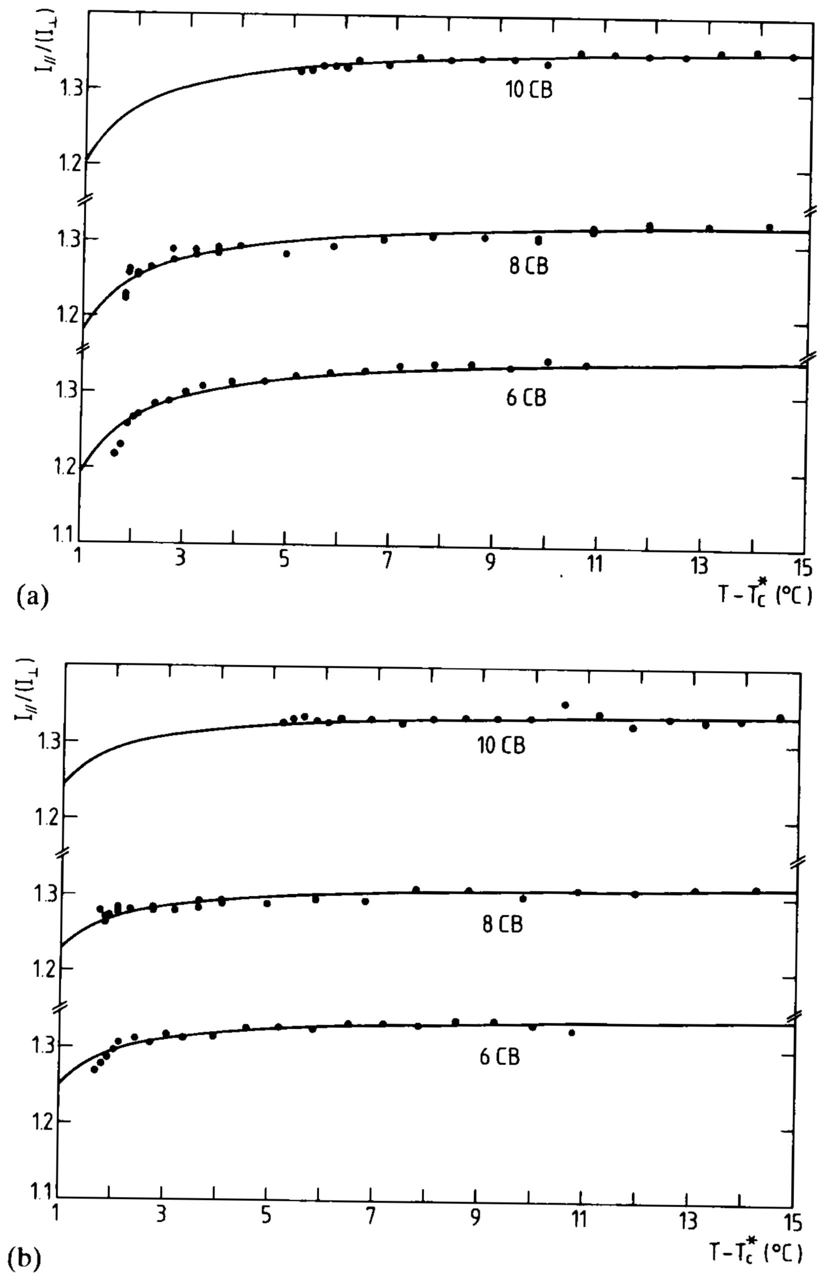

FIGURE 6 Depolarization ratios $I_{\parallel}/_{\perp}$ for 6CB, 8CB and 10CB at 488 nm for aperture a) A_1 = 1 mm and b) A_1 = 3 mm. Full curves according to Equation (13).

as observed by others.[3,7b] This is in agreement with measurements on the magnetic birefringence by Zhang *et al.*[8] We attribute reports of a different behaviour either to multiple scattering effects, or to an insufficient temperature stabilization leading to measurements in a two-phase region.

(ii) The difference between a nematic-isotropic and a smectic-isotropic phase transition shows up as a larger value of $T_c - T_c^*$ in the latter case (see Table I). In both cases the deviations of the light-scattering intensity from the $(T - T_c^*)^{-1}$ behaviour increases monotonically on approaching T_c. Hence, as the qualitative behaviour of the light-scattering is *not* different in the two situations, there is no need to include terms related to the smectic ordering in the Landau free energy.[4,16]

The experimental situation thus being established it seems worth while to compare them in some detail with the theoretical predictions, in particular with Equations (4) and (6). Considering the phase transition as a critical point where only the coefficient A in the Landau theory changes sign, the following relations can be derived:[1,11]

$$a = 3\frac{\Delta H}{T_c S_c^2}, \tag{15a}$$

$$B = -27\frac{\Delta H}{T_c S_c^3}(T_c - T_c^*), \tag{15b}$$

$$c = 9\frac{\Delta H}{T_c S_c^4}(T_c - T_c^*), \tag{15c}$$

where ΔH is the latent heat associated with the phase transition, and S_c the value of the scalar order parameter at T_c. Neglecting terms of order S^3 and higher, the elastic coefficients L_1 and L_2 are related to the nematic elastic constants K_1, K_2 and K_3 via

$$K_1 = K_3 = (2L_1 + L_2)S^2 \tag{16a}$$

$$K_2 = 2L_1S^2 \tag{16b}$$

or at T_c where S is small and the approximation is best:

$$\overline{L} = \overline{K}_c/(2S_c^2). \tag{16c}$$

A full set of data can be obtained for 8CB:

- $T_c = 40.42°\mathrm{C}$,
- $S_c = 0.395$ (Reference 17),
- Latent heat 612 J/mol (Reference 18), normalised with a density of 0.98 g cm^{-3} and a molecular weight of 290.5 to $\Delta H = 2.06 \times 10^6$ J m^{-3},
- elastic constants at T_c[19]

$$K_1 = 2.4 \times 10^{-12}\ \mathrm{N}$$

$$K_2 = 1.2 \times 10^{-12}\ \mathrm{N}$$

$$K_3 = 2.6 \times 10^{-12}\ \mathrm{N}$$

This leads to (energies in 10^{-21} J, distances in 10^{-9} m, temperatures in K):

$$\begin{aligned} k_BT_c &= 4.33 \\ q_m &= 4.94 \text{ (Debye value)}, \\ a &= 0.126, \\ B &= -2.88\,(T_c - T_c^*), \\ C &= 2.43\,(T_c - T_c^*), \\ \bar{L} &= 6.62. \end{aligned} \tag{17}$$

In fact for the ratio L_2/L_1 a value of about 2 is obtained. A least-squares procedure was adopted to fit the light-scattering data to Equation (6) using the figures of Equation (17) and T_c^* as an adjustable parameter. An enlarged view of the neighbourhood of T_c is shown in Figure 7. The theoretical curve (broken line) does not explain the curvature in the experimental data. The only significant difference to the Gaussian approximation is a reduction of $T_c - T_c^*$ by a factor 30.

The source of the discrepancy between theory and experiment might be in the Debye value taken for the momentum cut off q_m. In fact, using this value means that order parameter fluctuations are considered up to a molecular scale, where continuum theory fails.

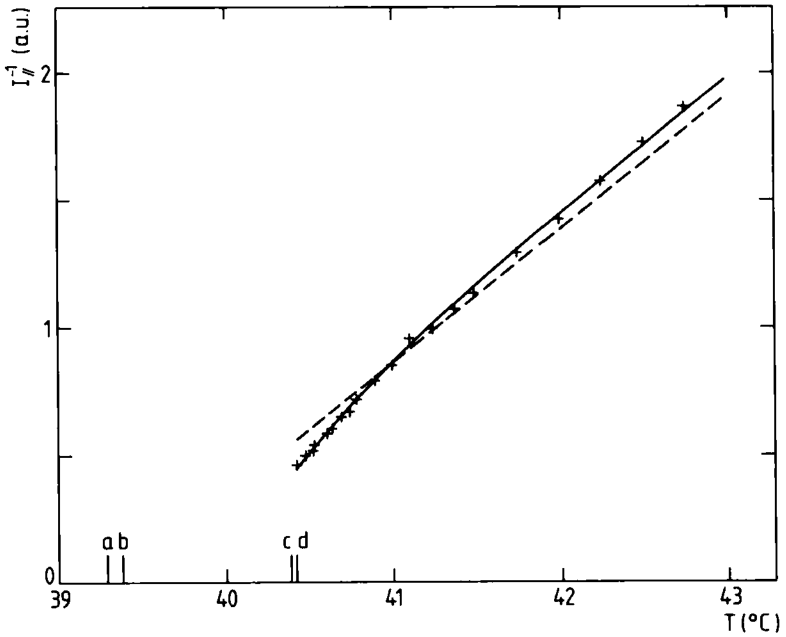

FIGURE 7 Enlarged portion of Figure 2. Theoretical curves are according to Equation (6), broken line: Debye cut-off for q_m, full line: best fit for q_m. Location of T_c^*: a) best fit for q_m, b) Gaussian approximation, c) Debye q_m, d) location of T_c.

Hence, though in principle q_m should be well-defined and fixed, in a liquid of anisotropic molecules there is some ambiguity about the proper value. Because of short-range correlation (clustering of molecules) use of a lower q_m-value could be justified. The correct value cannot be derived from the foregoing theory, as would be the case for a solid crystal. X-ray measurements in the nematic phase indicate clusters of 5–10 molecules.[20] Sheng[21] derived from nematic director fluctuations in *p*-azoxyanisole by Luckhurst[22] the order of magnitude $q_m \approx 0.6 \times 10^9\ \mathrm{m}^{-1}$. This is in the neighbourhood of the reciprocal molecular length $\ell^{-1} \approx 0.5 \times 10^9\ \mathrm{m}^{-1}$ and some 10 times below the Debye values.

Keeping q_m as an adjustable parameter we found for 8CB a good fit with the experiments for $q_m = 0.25 \times 10^9\ \mathrm{m}^{-1}$ (see Figure 7, full line). This is also close to ℓ^{-1} and some 20 times below the Debye value. Table II gives some calculated values for $T_c - T_c^*$, which quantity turns out to be very sensitive to the choice of q_m. The customary procedure of locating T_c^* by extending the straight line, as in Figure 2 is too simple. The agreement of $T_c - T_c^*$ from the Gaussian

TABLE II

Results for $T_c - T_c^*$ for different fits to the 8CB data using Equation (7)

$q_m/10^9\ \mathrm{m}^{-1}$	$T_c - T_c^*$°C
Gaussian approximation	1.04
4.94 (Debye value)	0.03
1.00	0.16
0.50	0.39
0.25 (best fit)	1.12

approximation and from our best fit, is purely accidental. For 5CB a similar value for q_m was found. Owing to the first order nature of the nematic-isotropic transition, the part of the critical region closest to the critical point is not accessible to the experiment. This causes relatively large uncertainties in the values of critical exponents, these being defined in this very region. Nevertheless there are indications, especially from the order parameter exponent β, that the nematic-isotropic phase transition should be viewed as a tricritical point.[23] In this case both A and C are zero at the phase transition, and a sixth order term has to be added to the Landau free energy to ensure stability. We have also fitted the light scattering data of 8CB to this situation, and arrive at a good fit for $q_m = 0.03 \times 10^9\ \mathrm{m}^{-1}$. This is an order of magnitude lower than ℓ^{-1} and probably corresponds to a nonphysical situation.

We conclude that pre-transitional light-scattering in the isotropic phase of 8CB is in good agreement with a model of the nematic-isotropic phase transition as a mean-field critical point, provided the reciprocal molecular length is used as momentum cut-off q_m. The latter choice is somewhat arbitrary, but nevertheless reasonable from the point of view that in X-ray measurements clusters of several molecules are observed. If one assumes critical behaviour one does not expect the results to be valid close to T_c^*. However, this region is experimentally not accessible. With a tricritical hypothesis the agreement is not as good. But as a tricritical hypothesis is supported by other critical exponents, one is forced to conclude that the nature of the nematic-isotropic phase transition is still not fully understood.

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