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Additional contribution, with no critical thermal behavior, to the optical Kerr constant of nematogens in their isotropic phases

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The authors report on optical Kerr effect measurements performed in the isotropic phase of the nematogen *p*-methoxy-benzoate-*p*-*n*-pentylbenzene. The optical Kerr constant is found to obey the well-known $(T - T^*)^{-1}$-type law near the isotropic-nematic transition temperature, but to *deviate* from it at higher temperatures. An argument is presented for the existence of a roughly temperature-independant mechanism involved in the response of isotropic phases of nematogens to an intense electric field. A possible microscopic interpretation is suggested.

I. INTRODUCTION

The isotropic phase of a liquid crystal is a macroscopically disordered medium. But at a given time and a given point, there exist intermolecular orientational correlations, the extension and lifetime of which increase drastically in the vicinity of the isotropic-nematic transition. Rayleigh scattering and the optical Kerr effect are techniques very well suited for the study of the amplitude and dynamics of such correlations.

The optical Kerr effect belongs to nonlinear optics. However, it is well known that it is fundamentally related, through the fluctuation-dissipation theorem (see Appendix A), to the fluctuations of the optical anisotropy of the system at equilibrium and, consequently, to Rayleigh scattering.[1] This point of view will be detailed in Sec. II, on the basis of the de Genne's theory of the isotropic-nematic transition.[1] According to this theory, the intensity of the scattered light, the amplitude and relaxation time of the electrically induced birefringence should vary as a function of temperature as $(T - T^*)^{-\alpha}$. T^* is a virtual second-order transition temperature slightly below the temperature T_K of the isotropic-nematic transition, which is weakly first order, and α is a critical exponent which is equal to 1 in a mean-field theory such as that of Maier and Saupe.[2,3]

In the past few years, several authors have published experimental results in good agreement with this law for $\alpha = 1$. However, some values of α less than 1 have been reported, without comments. Particularly, Prost and Lalanne[4] pointed out that the Kerr constant of MBBA varies as $(T - T^*)^{-1/2}$. No viable explanation was ever given for this so-called anomaly, although the experimental setup of Prost and Lalanne suffered some technical imperfections. Thus it seemed to us interesting to repeat their work, with improved experimental technique and data analysis. The characteristics of our experimental setup and of the compound studied p-methoxy-benzoate-p-n-pentylbenzene (MBPB) are described in Sec. III. In Sec. IV, we examine the validity of some data analysis methods and give the results obtained for the optical Kerr constant and relaxation time of the induced birefringence in the isotropic phase of MBPB. Finally, Sec. V is devoted to the discussion of the thermal variations of the Kerr constant of liquid crystals in their isotropic phases. Particularly, we propose a qualitative explanation for the so-called anomaly previously reported.

II. PROBLEM

A. Landau-De Gennes theory of the isotropic-nematic transition

It is well known that the nematic phase of a liquid crystal is constituted of anisotropic molecules, nearly parallel to a common direction $\hat{n}$, but having their centers of mass randomly distributed. Macroscopically, the medium is uniaxial. Several experimental investigations have shown that the molecular permanent dipoles are practically uncoupled.[5] Then the crystal is of quadrupolar symmetry.

A microscopic order parameter describing the quality of the orientational correlations between the molecules is given by[1]:

$$Q_{\alpha\beta} = \tfrac{1}{2} S (n_\alpha n_\beta - \delta_{\alpha\beta}) ,$$

where n_α is the component of the local optical axis $\hat{n}$ along the direction $\hat{\alpha}$ of a referential linked to the laboratory and S is the scalar order parameter. Let be θ the angle between $\hat{n}$ and the direction of the highest molecular polarizability. Then

$$S=\tfrac{1}{2}\langle 3\cos^2\theta-1\rangle .$$

Beyond a temperature T_K, the value of S falls to zero discontinuously and the medium becomes macroscopically isotropic: the nematic-isotropic phase transition is first order.

When T decreases toward T_K, fluctuations develop, giving rise to a local instantaneous order which prefigures the nematic phase. These fluctuations are characterized by a lifetime τ and a geometrical extension measured by the correlation length ξ. Such microscopic or *dynamic* data can be obtained from the power spectra of the fluctuations in light scattering experiments. The amplitude of these fluctuations, which is a *static* property of the medium obtainable from the total scattered intensity, can be obtained as well through the measurement of such macroscopic quantities as the birefringence induced by a magnetic or electric field: this is a consequence of the fluctuation-dissipation theorem (see Appendix A). Using this theorem, we give the mathematical relations between the Kerr or Cotton-Mouton effects and the Rayleigh scattering in Appendix B.

Let us now briefly review the de Gennes theory of the isotropic-nematic transition. The free energy per unit volume is developed as a function of the powers of temperature and order parameter:

$$F=F_0+\tfrac{1}{2}AQ_{\alpha\beta}Q_{\beta\alpha}-\tfrac{1}{3}BQ_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha}+\tfrac{1}{4}CQ_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\delta}Q_{\delta\alpha}$$
$$-\tfrac{1}{3}\chi_{\alpha\beta}H_\alpha H_\beta+\tfrac{1}{2}L_1\partial_\alpha Q_{\beta\gamma}\partial_\alpha Q_{\beta\gamma}+\tfrac{1}{2}L_2\partial_\alpha Q_{\alpha\gamma}\partial_\beta Q_{\beta\gamma}, \quad (1)$$

where H is a magnetic or electric field, $\chi_{\alpha\beta}$ is the corresponding susceptibility, and $Q_{\alpha\beta}$ is a new order parameter defined from macroscopic data only, such as

$$\chi_{\alpha\beta}-\tfrac{1}{3}\chi_{\alpha\alpha}\delta_{\alpha\beta}=\tfrac{2}{3}\Delta\chi Q_{\alpha\beta}, \quad (2)$$

where $\Delta\chi$ is the difference $\chi_\perp-\chi_\parallel$ of the eigenvalues of $\chi_{\alpha\beta}$ for the perfectly aligned medium ($S=1$). L_1 and L_2 are elastic constants and describe the increase in free energy associated with a gradient of order in the medium. They are simply related to the correlation length of the fluctuations of the order parameter,

$$\xi^2\sim(1/A)(L_1+\tfrac{1}{6}L_2);$$

ξ is usually very small compared to the visible wavelengths.[6-8] As it will be shown in Sec. IV, a consequence of this property is that the elastic terms are completely negligible in the optical Kerr effect. The coefficient A is assumed to vary as

$$A=a(T-T^*)^\alpha,\quad \alpha>0 .$$

B and C should remain constant. The transition occurs at a temperature T_K slightly above T^* obtained from

$$a(T_K-T^*)^\alpha=\tfrac{2}{27}B^2/C .$$

At $T=T_K$, S jumps from 0 to $S_K=\tfrac{2}{3}B/C$.

To express $Q_{\alpha\beta}$ as a function of $H_{\alpha\beta}$ and of time, one requires the knowledge of the hydrodynamic equations of the medium. de Gennes assumes the following system, where $Q_{\alpha\beta}$ is coupled with velocity gradients

$$-\frac{\partial F}{\partial Q_{\alpha\beta}}=\mu(\partial_\alpha V_\beta+\partial_\beta V_\alpha)+\nu\frac{\partial Q_{\alpha\beta}}{\partial t}, \quad (3)$$

$$\rho\frac{\partial V_\alpha}{\partial t}=\partial_\beta\sigma_{\alpha\beta}-\partial_\alpha p, \quad (4)$$

$$\tfrac{1}{2}\sigma_{\alpha\beta}=\tfrac{1}{2}\eta(\partial_\alpha V_\beta+\partial_\beta V_\alpha)+\mu\frac{\partial Q_{\alpha\beta}}{\partial t}, \quad (5)$$

where $\sigma_{\alpha\beta}$ is the dissipative part of the stress tensor, p the pressure and ρ the mass per unit volume. The coefficients μ, ν, and η have the dimension of the viscosity. This coupling can be revealed by means of a static flow gradient $\partial V_x/\partial y$. A "flow birefringence" results from this constraint:

$$\Delta n=\tfrac{2}{3}\mu\frac{\Delta\epsilon}{nA}\frac{\partial V_x}{\partial y},$$

where n is the refractive index and $\Delta\epsilon$ is defined according to expression (2) for the dielectric permittivity. In the case of the optical Kerr effect, and when there is no flow constraint, we may ignore the coupling between $Q_{\alpha\beta}$ and the velocity gradients (see Appendix C). The following simplified equation may then be used

$$-\frac{\partial F}{\partial Q_{\alpha\beta}}=\nu\frac{\partial Q_{\alpha\beta}}{\partial t}.$$

Let us now assume that a linearly polarized electric field E of circular frequency ω_I is applied to the medium. In the following we shall consider the frame (x, y, z) defined by $\hat{z}$, the direction of propagation of the field, and $\hat{y}$, the direction parallel to the electric field. The birefringence $\Delta n=n_x-n_y$ induced at the probe circular frequency ω_p is then given by the convolution product

$$\Delta n_p=(2\pi c/\omega_p)B(\omega_p,\omega_I)E^2\times f, \quad (6)$$

with the following notations: $B(\omega_p,\omega_I)$ is the optical Kerr constant,

$$B(\omega_p,\omega_I)=(\omega_p/cn_p)\Delta\chi(\omega_p)\Delta\chi(\omega_I)/A, \quad (7)$$

$n(\omega_p)$ is the refractive index at the probe circular frequency, c is the velocity of light, and f is the impulse response of the system:

$$f(t)=(A/\nu)y(t)\exp(-At/\nu)\,. \tag{8}$$

From Eqs. (6) and (8) we deduce the following expression for the spectrum of the light scattered by the fluctuations of $Q_{\alpha\beta}$ (see Appendix B):

$$I_{xx}(\omega)=\tfrac{4}{3}I_{xy}(\omega)$$
$$=\tfrac{16}{27}kT(\Delta\epsilon)^2(1/A)\Gamma/(\Gamma^2+\omega^2)\,.$$

Since $\Gamma=A/\nu$, both the whole scattered intensity and the inverse Γ^{-1} of the width of the related spectrum vary as $(T-T^*)^{-\alpha}$.

The theoretical prediction of the value of α requires a microscopic description of the system, allowing the calculation of the angular correlation parameter J_A introduced by Kielich *et al.*[9] The link with de Gennes's phenomenological theory is then ensured, for instance, by the microscopic expression of the optical Kerr constant:

$$B(\omega_p,\omega_I)\propto\gamma(\omega_I)\gamma(\omega_p)(1+J_A)\,,$$

where $\gamma(\omega_I)$ and $\gamma(\omega_p)$ are the anisotropies of the first-order molecular polarizability at the circular frequencies ω_I and ω_p.

Let us recall that such a mean-field theory as that of Maier and Saupe[2,3] leads to

$$J_A\propto 1/(T-T^*)\,,$$

that is,

$$\alpha=1\,.$$

The few experimental methods that we have discussed in this section appear as easy means of access to the coefficient A of Eq. (1) and then to both T^* and the critical exponant α.

B. Experimental results

1. Dynamic properites

The first measurements of the correlation time $\tau=\nu/A$ were performed on *p*-methoxy-benzilidene-*p*-*n*-butylaniline (MBBA) by Stinson and Litster[6,7] by means of Rayleigh scattering. They pointed out that τ varies as $(\nu/a)(T-T^*)^{-1}$ provided that the coefficient ν is assumed to vary with T as the shear viscosity η. Moreover, they have shown that the correlation length ξ was very small compared to the optical wavelengths, in good agreement with de Gennes's estimate. Most recently they have studied the influence of the coupling of the order parameter to the shear modes of the liquid,[8] using the depolarized spectrum $I_{xy}(q,\omega)$; it seems that their results can be explained by de Gennes's hydrodynamic equations up to several degrees above the transition. Some other measurements of τ were performed on various compounds, using the optical Kerr effect[4,10-12] and, recently, the relaxation of electrically induced birefringence.[13] In every case, the observed behaviors were in good agreement with the mean-field law.[14]

2. Static properties

Let us briefly review the results obtained with the above-mentioned techniques.

a. Rayleigh scattering. Once again, the pioneering work is that of Stinson and Litster.[6-8] They concluded that the behavior of the scattered intensity was that predicted by the mean-field model, except when T is close to T_K, where this intensity increases "irregularly": it seems that in the vicinity of the transition, the contribution of order-parameter fluctuations to the free energy is no longer negligible and that the mean-field approximation is no longer applicable.

b. Cotton-Mouton effect. Stinson and Litster[7,8] have measured the Cotton-Mouton constant of MBBA and found it to vary with temperature exactly as the scattered intensity. Different conclusions were reported by Filippini and Poggi,[15] who claimed that the Cotton-Mouton constant of such compounds as *p*-ethoxy-benzilidene-*p*-*n*-butylaniline (EBBA), MBBA, and 4-cyano-4-heptyl biphenyl vary proportionately to $(T-T^*)^{-1}$ only up to a temperature T_1 about ten degrees above T_K. Beyond T_1 there is an increasing departure from the mean-field law.

c. Static Kerr effect. The static Kerr effect approach is a rather less easy technique to use, since it involves two different microscopic mechanisms: (i) The coupling between the electric field and the induced dipoles which is the only one involved in Cotton-Mouton and optical Kerr effects and which is accounted for in the theory reviewed above. The related macroscopic response varies as $(T-T^*)^{-\alpha}$. (ii) The coupling between the electric field and the permanent dipoles. Onsager's local-field correction leads to a contribution proportional to $\mu^2(3\cos^2\beta-1)/kT(T-T^*)^{\alpha}$, where β is the angle between the dipole μ and the axis of highest molecular polarizability.[16] Measurements of the static Kerr constants of several *p*-*p'*-*n*-alkoxyazoxy benzene homologous compounds were reported recently by Bischofberger *et al.*[16] They have found good agreement with the aforementioned assumptions, with $\alpha=1$, and deduced the values of β for each compound.

When $3\cos^2\beta-1<0$ the compound is said to be of "negative anisotropy." The negative dipolar term predominates only at low temperature. Therefore the sign of the Kerr constant is expected to change when one increases the temperature.

This was observed experimentally by Tsvetkow and Ryumtsev[17] for *p*-azoxy-anizole (PAA). When $3\cos^2\beta - 1 > 0$ ("positive-anisotropy" materials), both contributions act in the same way. Thus the Kerr and the Cotton-Mouton effects should lead to similar conclusions. Consequently, one may be surprised by the results that Schadt and Helfrich[18] reported in 1972 for *p*-ethoxybenzilidene-*p*-amino-benzonitrile (PEBAB): $\alpha = 0.51 \pm 0.05$ and $T_K - T^* < 0.2$ °K. But, one year later, Johnston[19] found $\alpha = 1$ for the same compound and other positive ones. And recently Schadt's study of a series of alkylcyanophenylpirimidines[13] demonstrated good agreement with the mean-field law.

d. Optical Kerr effect. Because of the short duration of the perturbation some slow parasitic phenomena are eliminated, like electrostriction or electrocalorific effects. Moreover, since the optical field does not couple with permanent dipoles, every nematogen, whether positive or negative, may be studied by means of such a technique with equally good conditions for interpretation. Moreover, both τ and B are available from only one signal. Thus, among the perturbative methods the optical Kerr effect is a powerful tool, equivalent to Rayleigh scattering. Paradoxically, the results obtained by Stinson and Litster from Rayleigh scattering were not confirmed by the optical Kerr effect experiment performed by Lalanne and Prost on MBBA in 1971.[4] The latter did verify the validity of the mean-field law in the case of relaxation time, but found that the optical Kerr constant of MBBA varies as $(T - T^*)^{-1/2}$. However, a similar experiment was performed later by Wong and Shen[10]; this time both the study of the relaxation time and that of the optical Kerr constant led to $\alpha = 1$. This conclusion was corroborated by further studies of series of *p*-*p*′-di-*n* alkoxyazoxy benzene,[12] of MBBA,[20] and of cyanobiphenyl homologues.[21]

e. Flow birefringence. Measurements of flow birefringence reported by Martinoty *et al.*[22] for MBBA and *p*-*n*-pentyl-*p*′-cyanobiphenyl (PCB), show good agreement with the law $(\mu/a)(T - T^*)^{-1}$, where the coefficient μ is assumed to vary with temperature according to an arrhenius law.

C. CONCLUSION

It is clear that in most reported cases experiments agree both with de Gennes's theory and the mean-field approximation. Wong and Shen[10] tried to attribute the anomalous results of Prost and Lalanne to experimental inadequacies, namely the complex spatial and temporal structures of their inducing wave. Such an explanation does not seem satisfactory, and besides, no appropriate one was ever given for the discrepancies reported by Schadt and Helfrich[18] or Filippini and Poggi.[15] We think that the observed discrepancies originate from a more fundamental source, and so have undertaken to perform an optical Kerr effect experiment, with improved setup and data analysis.

III. EXPERIMENTAL PROCEDURE

A. Inducing wave

The inducing wave used by Prost and Lalanne[4] was provided by a Nd^{3+} glass laser Q switched by a rotating prism. The main drawback of this technique was a poorly reproducible temporal structure, involving numerical treatments of the data. The presence on the commercial market of bis-(4-dimethylaminodithiobenzil)-nickel[23] (BDN) as easly as 1974 allowed us to replace the rotating prism by a passive Q switching. This dye, characterized by a remarkable photochemical stability, supplanted the rather unstable species formerly used (cyanines). For a solution of BDN inside a chlorated derivative of methane or ethane the absorption recovery time has been found of ~6 ns.[24] In the case of a fairly short cavity ($L < 0.5$ m), this is probably long enough to avoid any partial phase locking of the cavity modes. We used a solution of BDN in chloroform, with a concentration of ~7 $\mu g\,cm^{-3}$. The absorbing cell was 5 mm thick and placed inside an afocal optical (diverging lens-concave mirror) system constituting the rear reflector of the cavity. This allows one to reduce the energy density inside the dye solution and then to increase its lifetime. At the same time the probability of parasitic stimulated effects (Raman, Brillouin) is decreased.

Figure 1(a) shows the recording of the temporal shape of a pulse. The detection system consisted of an RTC XA 1003 photocell coupled to a 7904-type Tektronix oscilloscope (bandwidth:2 GHz); the resulting impulse response was about 0.5 ns wide. The laser pulse shows no substructure and is very reproducible. Its temporal shape is well fitted by a Gaussian function with a 30-ns width at $1/e$.

The transverse structure of the inducing wave must also be highly reproducible. In fact, the amplitude of the signal related to the induced birefringence is proportional to

$$\int\int E_I^2(x,y)E_A(x,y)\,dx\,dy\,, \tag{9}$$

where (x, y) are the coordinates in a plane perpendicular to the common axis of the inducing and probe beams, E_I^2 is the intensity of the inducing beam, and E_A the amplitude of the probe field.

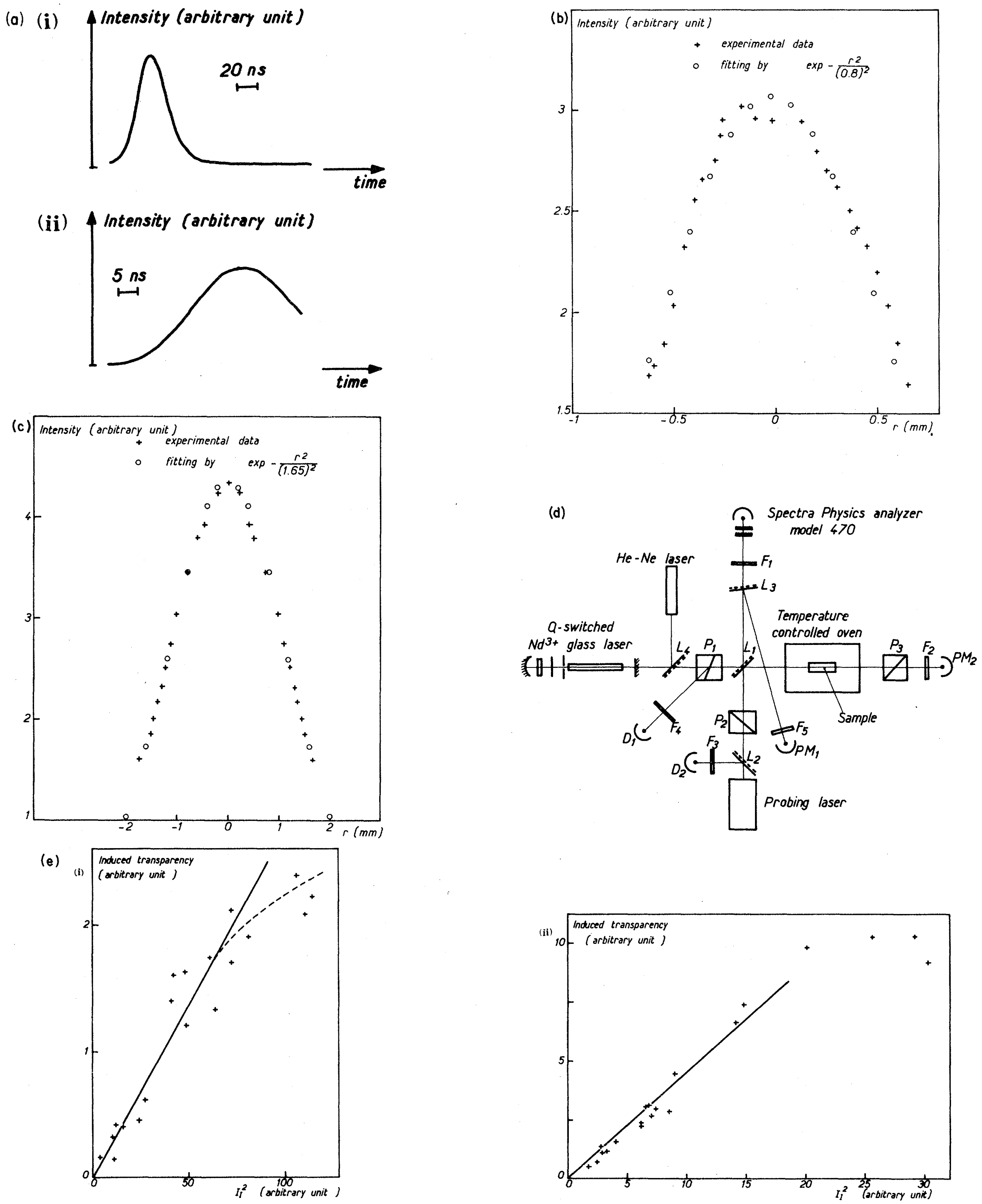

FIG. 1. (a) Temporal structure of an inducing pulse: (i) whole pulse, sweep time = 20 ns/div. (ii) rising part, sweep time = 5 ns/div. (b) Transverse structure of the infrared beam close to the output coupler. Filtering-hole diameter is 2 mm. + : experimental data; O: fitting by exp $[-r^2/(0.8)^2]$. (c) Transverse structure of the infrared beam at the location of the Kerr cell [see Fig. 1(d)], e.g., 1.5 m away from the laser. Filtering-hole diameter is 2 mm. + : experimental data; O: fitting by exp $[-r^2/(1.65)^2]$. (d) Optical Kerr effect setup. P_1, P_3: Glan prisms; P_2: Wollaston prism; $D_\perp$: CSF CPA 1443 photocell; D_2: Hewlett-Packard 5082-4207 photodiode; PM_1: *La* Radiotechnique 150 CVP photomultiplier; PM_2: *La* Radiotechnique XP 1002 or XP 2020 photomultiplier; F_1, F_3: MTO Athervex T_a filters; F_2: Oriel interference filter; F_4, F_5: MTO DIH 70b filters; L_1, L_2, L_3, L_4: beam splitters. (e) Proportionality of the induced transparency to I_I^2. (i) $\lambda_p = 632.8$ nm; (ii) $\lambda_p = 441.6$ nm.

TABLE I. Radius of the TEM_{00} mode at the exit of the laser.

Filtering-hole diameter (mm)	0.8	1	1.2	1.5	2
r_0 (mm) close to cavity exit	0.84	0.50	0.54	0.54	0.80

Usually $E_A(x,y)$ does not vary with time since it corresponds to the TEM_{00} mode of a cw gas laser, so we see that a simple condition for keeping the integral (9) constant is to use an exciting laser oscillating on the TEM_{00} mode. This output characteristic was obtained by inserting pinholes with diameters from 0.8 to 2 mm into the laser cavity. Figure 1(b) shows the transverse structures of the infrared beam recorded close to the exit of the laser cavity for a 2-mm filtering hole. The circles represent the fitting of the experimental data by a Gaussian function e^{-r^2/r_0^2} (theoretical shape of the TEM_{00} mode of a confocal cavity and more generally of a low-loss cavity[25,26]). Since we used a high-loss plane-plane cavity, we did not expect the TEM_{00} mode of our laser to be Gaussian close to the exit mirror.[27] Thus the value of r_0 (see Table I) must be considered only as the radius of the mode at $1/e$ of its maximum. But, as a consequence of Fresnel diffraction, the beam was expected to become nearly Gaussian at some distance away from the laser cavity. This behavior is illustrated in Fig. 1(c) and was an accurate tool for checking the reproducibility of the transverse structure of the inducing wave inside the Kerr cell. It proved to be very good indeed. The beam divergence for a 2-mm filtering hole is $\delta\theta = 0.6\times 10^{-3}$ rad. This value is close to the theoretical value of the far-field angle obtained for a Gaussian fundamental mode of beam waist r_0:

$$\lambda/\pi r_0 = 0.4\times 10^{-3} \text{ rad}$$

The natural complement to the study of the temporal properties of the inducing wave is that of its frequency spectrum. We used a Fabry-Perot interferometer, coated for the visible range. Thus we had to double the frequency of the laser by means of a KDP crystal. In most of cases, the spectra showed only one longitudinal mode, whatever might be the electric voltage on the pumping flashes.[28] The average energy W of the pulses, for a 2-mm filtering hole was ~2 mJ.

Using for the transverse and temporal distribution of the laser field the expression

$$E(r,\theta,t) = E_0 e^{-r^2/r_0^2} e^{-t^2/2\delta^2},$$

we have calculated the value of E_0 for $2\delta = 30$ ns and $r_0 = 0.8$ mm, and found it to be

$$E_0 \sim 5.3\times 10^6 \text{ V m}^{-1} \quad (\text{MKSA}),$$

or

$$E_0 \sim 177 \text{ statvolt cm}^{-1} \quad (\text{esu}).$$

B. Probing laser and detection of induced birefringence

A first experiment has been carried under the conditions of the Prost-Lalanne work, that is, with a probe beam of 632.8 nm delivered by cw helium-neon laser and a La Radiotechnique XP 1002 photomultiplier. An improvement was nevertheless afforded to the experiment by the use of a single-frequency He-Ne cw laser. Then we performed a second experiment with a faster detector (La Radiotechnique XP 2020). This photomultiplier has a maximum sensibility in the vicinity of 400 nm. We then replaced the helium-neon laser by a single-frequency helium-cadmium laser at 441.6 nm. The response characteristics of both XP 1002 and XP 2020 are summarized in Table II.

The impulse responses of both photomultipliers were studied by means of short light pulses: (i) Picosecond pulses, at $\lambda = 530$ nm, in the case of the XP 1002. The impulse response obtained by this technique is distinctly asymmetrical: one observes a quasilinear rising part followed by a clearly trailing relaxation, which can be fitted by a decreasing exponential with a characteristic time ~3.3 ns. (ii) Pulses of duration <0.9 ns delivered by a flash generator, in the case of the XP 2020. The response is then quasisymmetrical with no trailing tail.

It is clear from what preceeds that the shape

TABLE II. Response characterics of the photomultiplier tubes XP 1002 and XP 2020.

	Voltage (V)	Rise time	Standard deviation of transit time fluctuations (ns)	Width at half maximum (ns)
XP 1002	1800	4	4	
	1700			3.6
XP 2020	2500	1.5	0.3	2.4

of the induced birefringence signal will be less distorted by the XP 2020 photomultiplier than by the XP 1002. This rather than the small difference between the widths at half maximum, was the reason why we chose the XP 2020.

C. Compound studied: MBPB

MBBA, which was studied in the first optical Kerr effect experiments performed with liquid crystals,[4,10] is well known to be rather unstable and impure, so we replaced it by *p*-methoxy benzoate-*p*-*n*-pentyl-benzene (MBPB) (provided by Thomson-CSF company). Our sample stayed colorless for 18 months and was repurified only once, after our first experiment at 632.8 nm. Its mesomorphic properties are similar to those of MBBA:

$$\text{solid} \overset{29.0\ ^{\circ}\mathrm{C}}{\rightleftharpoons} \text{nematic} \overset{42.4\ ^{\circ}\mathrm{C}}{\rightleftharpoons} \text{isotropic.}$$

we have observed a slight decrease (~1 °C) in the isotropic-nematic phase transition temperature after one year. Besides, and contrary to MBBA, MBPB does not give rise to "dynamic scattering"[29]: the permanent dipolar momentum of the molecule is nearly parallel to its axis of highest polarizability. In such cases the compound is said to be "positive."

D. Optical Kerr effect setup

1. Inducing wave

The inducing wave is polarized outside the laser cavity by the Glan prism P_1 at 45° to the vertical. The reflected part of the beam is sampled by a fast photocell (CSF CPA 1443) which triggers the oscilloscopes. The characteristics of the infrared pulse are measured by means of the photomultiplier PM_1.

2. Temperature regulation

The sample is contained in a glass cell 4 cm long placed at the center of an oven, the temperature of which is kept constant by means of a regulator. The error signal is obtained from (i) a 2801-A Hewlett-Packard quartz thermometer in our first experiment at $\lambda_p = 632.8$ nm, and (ii) a platinum resistance thermometer in our second experiment, at $\lambda_p = 441.6$ nm. In both cases the temperature stabilization was better than $\pm 10^{-2}$ °C.

3. Probe beam

The amplitude of the probe beam at the instant of the shot is measured by means of a Hewlett-Packard 5082-4207 pin photodiode coupled to a Tektronix 7623 storage oscilloscope. The probe beam is vertically polarized by the Wollaston prism P_2, which is crossed with the Glan prism P_3.

4. Signal recording

The photomultipliers PM_1 and PM_2 are coupled to a one-beam Tektronix 7904 oscilloscope via two 7A19 amplifiers (input impedance: 50 Ω bandwidth: 500 MHz). The induced birefringence signal is shifted 75 ns back by means of a Tektronix 7M11 delay line. Then the two signals from PM_1 and PM_2 are added and visualized on the screen of the oscilloscope.

5. Compound absorption

The linearity of the setup at $\lambda = 1060$ nm was found to be better than ±5%. Table III gives the values of the absorption rate of MBPB at the three wavelengths used in the experiment.

6. Proportionality of induce birefringence to E_I^2

When the intensity E_I^2 of the inducing field increas-

TABLE III. Absorption rate of MBPB at the three wavelengths used.

						$\lambda = 632.8$ nm					
T (°C)	42	42.2	42.4	42.6	42.8	43	44	45	50	57	65
α (m^{-1})	4.38	4.08	3.45	2.93	2.70	2.68	1.74	1.44	1.40	1.11	0.14
						$\lambda = 441.6$ nm					
T (°C)	42.10	42.31	42.72	43.12	44.20	45.06	47.15	49.11	51.19	53.16	57.11
α (m^{-1})	32.10	24.0	14.78	12.08	7.58	7.58	3.40	3.56	3.20	2.40	2.02
						$\lambda = 1060$ nm					
T (°C)	42	42.2	42.4	42.6	42.8	43	44	45	50	57	63
α (m^{-1})	3.48	3.48	3.48	3.48	3.17	3.17	2.86	2.25	1.65	1.36	0.79

es, the induced birefringence Δn is no longer proportional to $B\lambda E_I^2$. This can be explained by the self-focusing phenomenon.[30] We shall not discuss here the numerous and complex mechanisms responsible for this effect. Let us simply recall that in the case of liquids with high Kerr constants, molecular reorientation plays the main role. Correlatively, parasitic nonlinear effects are generated (two-photons absorption, Raman and Brillouin stimulated effects), which dissipate part of the energy of the inducing wave. Besides, the quantity that one measures is not the induced birefringence Δn, but the induced transparency, given by

$$\sin^2\tfrac{1}{2}\Delta\psi = \sin^2[(\pi/\lambda)\Delta n] = \sin^2(\pi l B E_I^2),$$

where l is the length of the Kerr cell.

Figure 1(e) shows that, for the highest values of the infrared intensity I_I, the measured signal is no longer proportional to I_I^2. We may assume that $\sin^2\frac{1}{2}\Delta\psi$ can no longer be approximated by $\frac{1}{2}\Delta\psi^2$, but the divergence could also be attributed to self-focusing. We did not try to estimate the relative importance of these two contributions. The experiments have been performed with an inducing intensity low enough that the induced transparency is linear in I_I^2.

IV. DATA ANALYSIS AND RESULTS

We assume that the inducing and probe beams propagate along the direction $\hat{z}$ of a frame (x, y, z), and make the following definitions: l the length of the Kerr cell, α_p the absorption rate of the sample at the probe frequency, α_I the absorption rate of the sample at the inducing frequency, $I_I = E_I^2$ the intensity of the inducing wave, and I_p the intensity of the probe wave.

The birefringence induced in the Kerr cell at distance z and time t is given by

$$\Delta n(z, t) = B\lambda_p I_I(z, t)\times[f(t)\delta(r)],$$

where

$$f(t) = (1/\tau)y(t)e^{-t/\tau}, \quad \tau = \nu/A .$$

The induced transparency is

$$\sin^2\tfrac{1}{2}\Delta\psi \simeq (\tfrac{1}{2}\Delta\psi)^2,$$

with

$$\Delta\psi = \frac{2\pi}{\lambda_p} e^{-\alpha_p l/2}\int_0^l \Delta n(z, t)dz .$$

The orientational relaxation times involved in this experiment are at least of the order of several nanoseconds. Consequently, one may neglect the group effect[14,31] between the inducing and probe waves and reduce the variation of I_I along $\hat{z}$ to

$$I_I(t, z) = e^{-\alpha_I z} I_I(t) .$$

Then the probe intensity transmitted through the polarizer P_2 is

$$S_K(t) = I_p\{\pi B\rho[I_I(t)\times f(t)]\}^2 , \tag{10}$$

with

$$\rho = e^{-\alpha_p l/2}(1 - e^{-\alpha_I l})/\alpha_I .$$

Now let $R(t)$ be the impulse response of photomultiplier PM_2. The signal available from the experiment is then given by

$$S(t) = S_K(t)\times R(t) . \tag{11}$$

A. Measurement of relaxation time τ

Figures 2(a) and 2(b) are examples of the signals obtained for the two probe wavelengths used. The logarithm of the induced birefringence signal shown in Fig. 2(a) has been plotted in Fig. 2(c). This transformation was carried out for all the signals from our first experiment ($\lambda_p = 632.8$ nm). All the curves obtained in this way, for temperatures up to 55 °C, show a quasilinear decreasing part up to the vicinity of the maximum. Thus the relaxation times can be deduced directly by measuring the slopes of these straight lines.

Of course, this method does not take into account the distortion of $S_K(t)$ by the convolution product (11). This approximation can be validated as follows: the duration 2δ of the inducing pulse as well as the relaxation time τ involved in this experiment are always much larger than the width of the impulse response $R(t)$ of the photomultiplier. So $S(t)$ may be approximated by the first-order development

$$S(t) \simeq \int_{-\infty}^{+\infty}\left(S_K(t) - t'\frac{d}{dt}S_K(t)\right)R(t')dt' = S_K(t) - \epsilon\left(\frac{d}{dt}S_K(t)\right),$$

with

$$\epsilon = \int_{-\infty}^{+\infty} tR(t)dt .$$

Besides, when $t > 2\delta$, $S_K(t)$ is nearly proportional to $e^{-t/2\tau}$. Then

$$S(t) \simeq (1 + 2\epsilon/\tau)S_K(t) .$$

Thus the relaxation of the induced birefringence signal is not distorted by the photomultiplier and the aforementioned method—which we shall refer to as the "lorarithmic method"—is valid.

Figure 2(d) shows the variations versus tem-

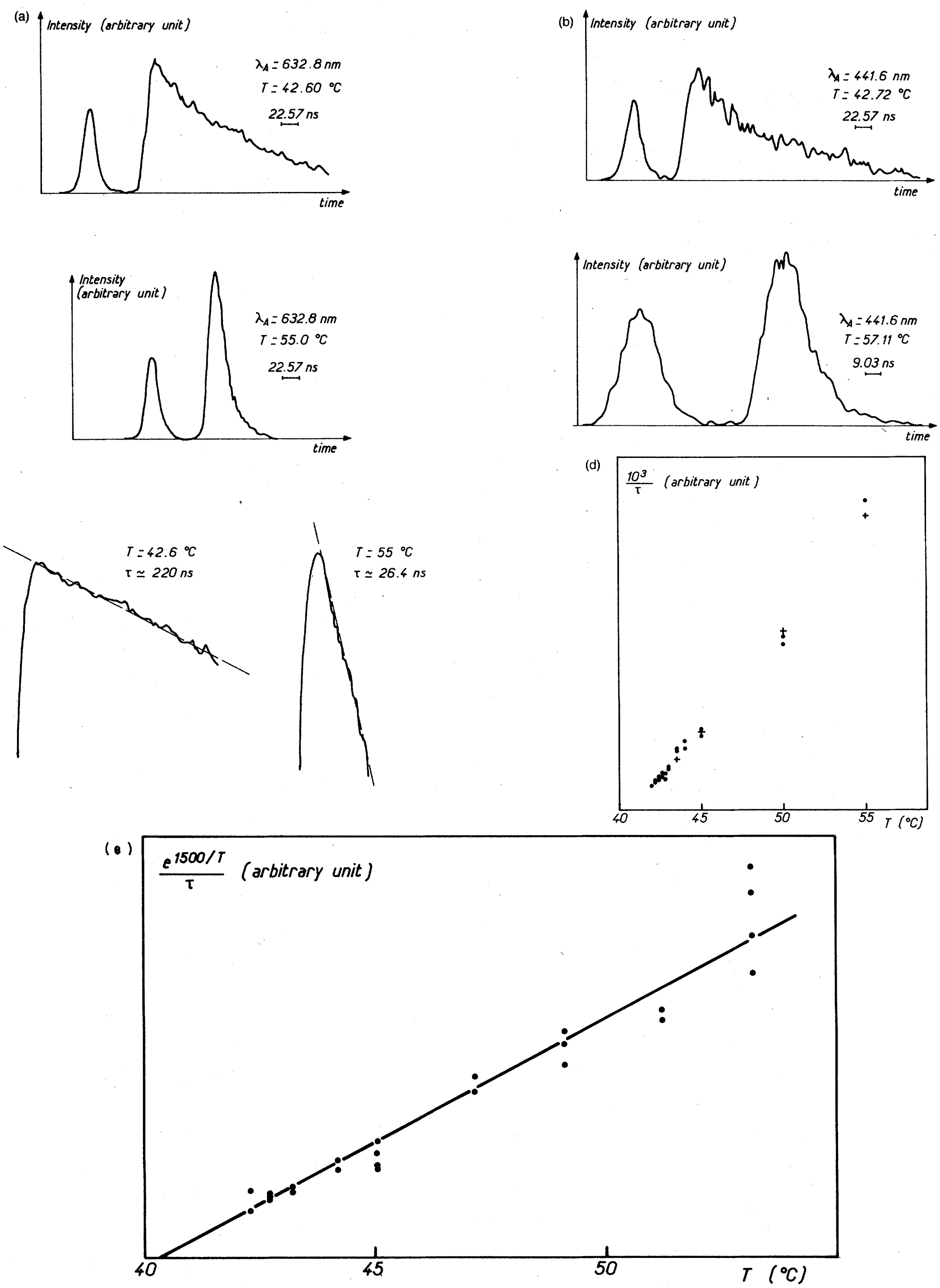

FIG. 2. (a) Inducing pulse and induced transparency signal. $\lambda_p = 632.8$ nm. (b) Inducing pulse and induced transparency signal; $\lambda_p = 441.6$ nm. (c) Logarithms of the signals of Fig. 2(a). (d) Inverse of relaxation time τ vs temperature, logarithmic method; $\lambda_p = 632.8$ nm. • experimental data; + fitting by $\tau = 4.17\ [\exp(1500/T)/(T - 313.69)]$. (e) $(1/\tau)\exp(1500/T)$ vs temperature (from the measurement of widths at half maximum); $\lambda_p = 441.6$ nm. (f) Inverse of the optical Kerr constant vs temperature, method "of maxima." (i) $\lambda_p = 632.8$ nm; (ii) $\lambda_p = 441.6$ nm. (g) Inverse of the optical Kerr constant vs temperature, "$\int S^{1/2}$" method. (i) $\lambda_p = 632.8$ nm; (ii) $\lambda_p = 441.6$ nm. (h) Inverse of the optical Kerr constant vs temperature, "$\int S$" method. (i) $\lambda_p = 632.8$ nm; (ii) $\lambda_p = 441.6$ nm.

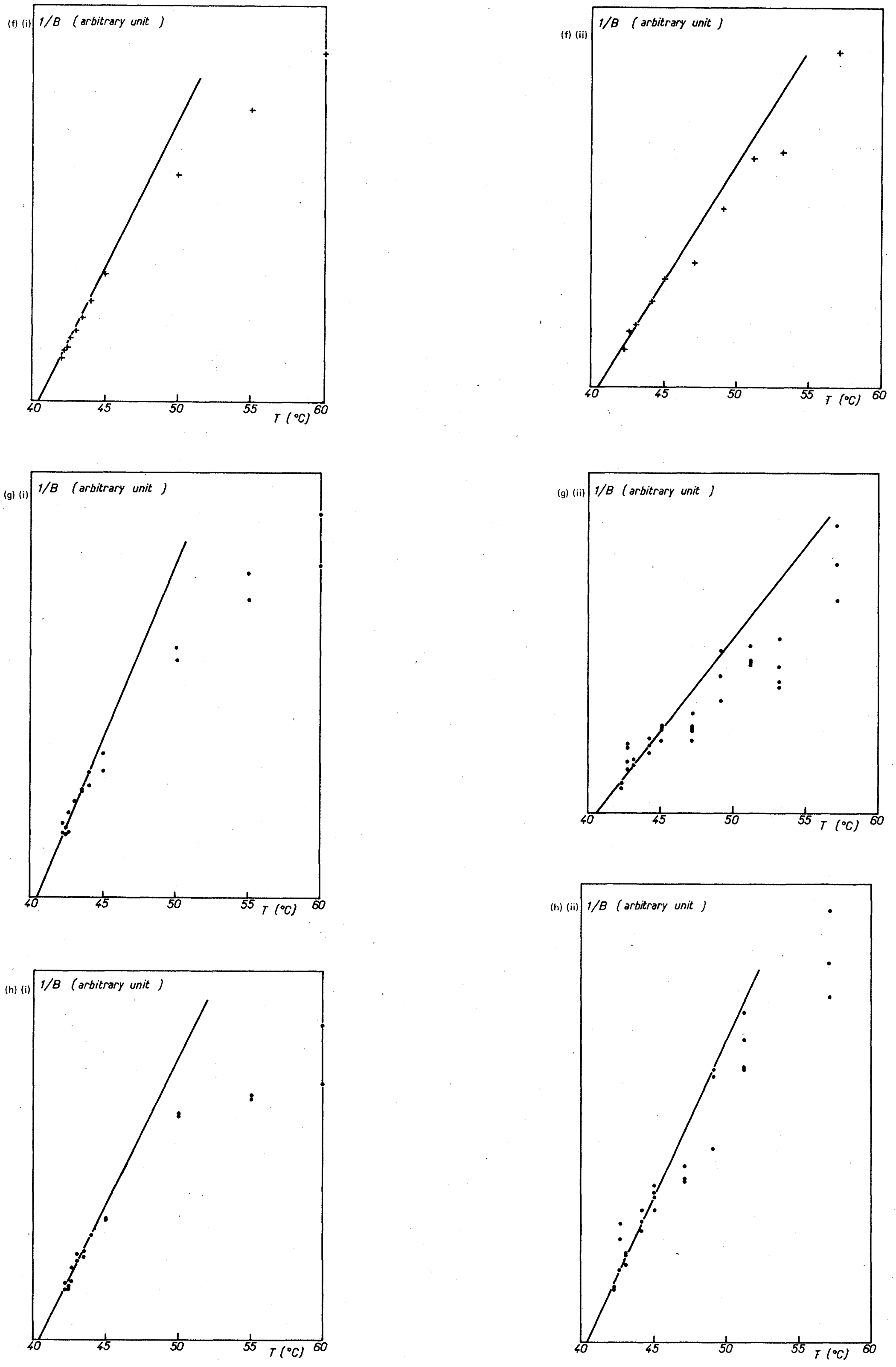

FIG. 2. (*Continued*)

perature of the inverse $1/\tau$ of the relaxation time obtained by the logarithmic method from our first experiment at $\lambda_p = 632.8$ nm. The curve is well fitted by

$$\tau_{ns} = 4.17 e^{1500/T}/(T - 313.69) .$$

The value of the activation temperature of the coefficient ν is in good agreement with that reported by Lalanne in an earlier paper[11] on MBPB. The virtual second-order transition temperature $T^* = 313.69$ °K $= 40.54$ °C, is about 2 °C less than the actual transition temperature T_K. The poor signal-to-noise ratio obtained in the second experiment made the measurement of τ by the logarithmic method difficult.

Then we chose another method, based on the measurement of the width at half maximum of the signals. Once again we neglect the convolution by $R(t)$ and assume the inducing intensity to be fitted by

$$I_I(t) = I_I e^{-t^2/\delta^2} .$$

Equation (10) can then be explicited as

$$S_K(t) = \tfrac{1}{4}\pi^3 I_p I_I^2 \delta^2 B^2 \rho^2 e^{\delta^2/2\tau^2} \times \left\{ \frac{1}{\tau} e^{-t/\tau} \left[1 + \operatorname{erf}\left(\frac{t}{\delta} - \frac{\delta}{2\tau} \right) \right] \right\}^2 . \tag{12}$$

The relation between τ and the width at half maximum has been computed numerically.

We have estimated the systematic error resulting from neglecting the response $R(t)$ of the photomultiplier XP 2020 and found it to be smaller than 8% at $T = 55$ °C.[32] This is less than the dispersion of the τ values obtained from a series of identical experiments performed at a given temperature. The results are given in Fig. 2(e).

Let us recall that the sample has been repurified between the two experiments. Within the experimental incertitude, neither T^* nor the values of τ were modified.

In conclusion, the thermal behavior of the relaxation time τ is found to obey the mean-field law $(\nu/a)(T - T^*)^{-1}$. The main interest of this study is to fix the value of T^* and therefore to eliminate an unknown parameter in the variation of the optical Kerr constant versus temperature.

B. Thermal variation of optical Kerr constant

We did not know *a priori* what could be the influence of neglecting the convolution by $R(t)$ in the determination of the optical Kerr constant. And the simple calculation reviewed above could not answer this question. So we chose to solve this problem empirically by using three different methods. Only the third one takes into account the convolution of $S_K(t)$ by $R(t)$.

1. Method "of maxima"

One compares the amplitude of the maximum of the recorded signal to the same amplitude calculated numerically from Eq. (12) for the corresponding value of τ. The principle of this method is close to that already used by G. K. Wong and Y. R. Shen,[10] who measure the amplitude of the signal at the time when the inducing pulse is maximum. The results obtained from the two experiments performed, are shown in Fig. 2(f), where $1/B$ is plotted versus temperature.

2. "$\int S^{1/2}$" method

This is the direct method previously used by Prost and Lalanne[4] for studying the optical Kerr constant of MBBA. The convolution of $S_K(t)$ by $R(t)$ is neglected. Thus

$$\int_{-\infty}^{+\infty} [S(t)]^{1/2} dt = I_p^{1/2} \pi B \rho \int_{-\infty}^{+\infty} I_I(t) dt .$$

This formula requires neither a value of τ nor any assumption about the shape of the inducing pulse. Moreover, the value of $\int_{-\infty}^{+\infty} I_I(t)dt$ is accessible without any approximation, whatever may be the impulse response of the photomultiplier PM_1. The results obtained from this method are shown in Fig. 2(g).

3. "$\int S$" method

The simplest way to take into account the convolution of $S_K(t)$ by $R(t)$ is to perform the integration of $S(t)$:

$$\int_{-\infty}^{+\infty} S(t) dt = \int_{-\infty}^{+\infty} S_K(t) dt = I_p (\pi B \rho)^2 \int_{-\infty}^{+\infty} [I_I(t) \times f(t)]^2 dt .$$

The analytical form of $S_K(t)$ must be known to evaluate this integral. From Eq. (12), and after some algebra, one finds

$$B^2 = \left[2 \left(\int_{-\infty}^{+\infty} S(t) dt \right) \tau e^{-\delta^2/2\tau^2} \right] \Big/ \left[\pi^{3/2} I_p \left(\int_{-\infty}^{+\infty} I_I(t) dt \right)^2 \rho^2 \left(\int_{-\infty}^{+\infty} e^{-t^2} [1 + \operatorname{erf}(t - \delta/\tau)] dt \right) \right] .$$

The integrals $\int_{-\infty}^{+\infty} e^{-t^2}[1+\mathrm{erf}(t-\delta/\tau)]dt$ have been computed numerically. The results for the optical Kerr constant are given in Fig. 2(h).

4. Conclusion

The aforementioned three methods give results which coincide within the dispersion of the measured values. *Each graph of $1/B$ as a function of temperature shows a definite curvature,* especially in the case of the first experiment ($\lambda_p = 632.8$ nm). The variation with temperature of the optical Kerr constant of MBPB, as measured by us, cannot then be fitted by a $(T-T^*)^{-1}$-type function. A consequence of these results is that they confirm the validity of the treatments chosen by Prost and Lalanne,[4] and by Wong and Shen.[10]

C. Absolute value of optical Kerr constant of MBPB

Carbon disulfide was used as a standard. The orientational relaxation time of CS_2 is extremely short (~2 ps),[33] and the corresponding impulse response may then be considered as a Dirac function $\delta(t)$. Therefore

$$S_K(t) = I_p[\pi B \rho I_I(t)]^2 .$$

To deduce B from $S(t)$, one must now take into account the time response of the detector:

$$\int_{-\infty}^{+\infty} S(t)dt = \int_{-\infty}^{+\infty} S_K(t)dt .$$

Once again $I_I(t)$ is fitted by $I_I e^{-t^2/\delta^2}$ and $B(CS_2)$ is given by

$$B^2(CS_2) = \left(\sqrt{2}\delta \int_{-\infty}^{+\infty} S(t)dt\right) \Big/ \left[\pi^{3/2}\left(\int_{-\infty}^{+\infty} I_I(t)dt\right)^2 I_p \rho^2\right] .$$

The negligible absorption of CS_2 at the two wavelengths involved in the experiment, $\lambda_I = 1060$ nm and $\lambda_p = 632.8$ nm, leads to

$$\rho \simeq 1 = 0.04 \text{ m} .$$

The temperature of MBPB was 45 °C and the relative value of its optical Kerr constant B was measured by the "$\int S$" method. This experiment was performed 12 months after the purification of the compound. We do not know what the influence of this delay on the value of B could be, but note that in the meanwhile T^* had slightly decreased (~-1 °C). We found that

$$B(\text{MBPB}) = 43 B(CS_2)$$

for $\lambda_I = 1060$ nm and $\lambda_p = 632.8$ nm. $B(CS_2)$ was measured by Paillette[34] for $\lambda_I = 694.3$ nm and $\lambda_p = 488$ nm:

$$B(CS_2) = 418.\ 10^{-9} \text{ esu} .$$

The following "microscopic" formula[35] allows us to calculate $B(CS_2)$ for $\lambda_I = 1060$ nm and $\lambda_p = 632.8$ nm:

$$B(\lambda_I, \lambda_p) = (6\pi\rho/45kT) n_p^{-1} \lambda_p^{-1} \cdot [\tfrac{1}{2}(n_I^2+2)]^2 [\tfrac{1}{3}(n_p^2+2)]^2 \gamma_I \gamma_p (1+J_A) , \tag{13}$$

where ρ is the number of molecules per unit volume, k is Boltzmann's constant, J_A an angular correlation parameter,[9] and γ the anisotropy of first-order molecular polarizability, which is also a dispersive quantity. We assume it to vary according to Havelock's law[36]:

$$\gamma^2(\omega) \propto [(n^2(\omega)-1)/(n^2(\omega)+2)]^4 .$$

Thus one finds, for $\lambda_I = 1060$ nm and $\lambda_p = 632.8$ nm,

$$B(CS_2) = 266.4 \times 10^{-9} \text{ esu}$$

and

$$B(\text{MBPB}) = 114.6 \times 10^{-7} \text{ esu}$$
$$= 12.7 \times 10^{-13} \text{ MKSA}$$

for $T - T^* = 5.5$ °C, $\lambda_I = 1060$ nm, and $\lambda_p = 632.8$ nm.

D. Determination of coefficients *a*, *b*, and *c* of Landau-De Gennes expansion

In Sec. IV B, it was pointed out that the thermal behavior of the optical Kerr constant of MBPB does not obey the $(T-T^*)^{-1}$-type law, especially in the high-temperature range. But for temperatures not exceeding the T_K value by more than 3 or 4 degrees, and where $\lambda_I = 1060$ nm and $\lambda_p = 632.8$ nm, we may write

$$B \simeq (2\pi/n\lambda_p)\Delta\chi(\omega_p)\Delta\chi(\omega_I)/9a(T-T^*)$$
$$= B_0/T - T^* = 0.73 \times 10^{-4}/(T-T^*) \text{ esu.}$$

Let Δn_K be the discontinuity of the refractive-index anisotropy at the transition. Then, to first order in Q_K,

$$\Delta n_K = (2\pi/\bar{n})\Delta\chi S_K ,$$

where $\bar{n}$ is the mean value of the refractive index at $T = T_K$,

$$\bar{n} = \tfrac{1}{3}(n_e + 2n_0) ;$$

$\bar{n}$ was measured at $\lambda = 632.8$ nm by means of a wedge method,[37] and found to be $\bar{n} = 1.5799$.

The dispersion of $\Delta\chi$ between ω_I and ω_p is probably small compared to the uncertainty in the determination of B_0. Then

$$a \simeq \frac{\bar{n}}{2\pi\lambda_p} \frac{1}{9B_0} \left(\frac{\Delta n_K}{S_K}\right)^2 .$$

Deduction of $\Delta n_K/S_K$ from refractive-index measurements requires a local-field model. We chose Vuks's model,[38] which has the advantage of great simplicity and seems to be more reliable than Neugebauer's.[39] $\Delta n_K/S_K$ is now given by[38]

$$\Delta n_K/S_K=\tfrac{4}{3}\pi N\Delta\alpha\,\frac{(\overline{n^2}+2)}{(n_e+n_0)}\,,$$

where N is the number of molecules per unit volume, in the nematic phase. At $T=T_K$ we have found $N=2.145\times10^{21}\ \mathrm{cm}^{-3}$. $\Delta\alpha$ is the anisotropy of polarizability of the molecule, which is assumed to be a symmetrical top. The value of $\Delta\alpha$ was known from depolarized Rayleigh scattering measurements performed at $\lambda=541.6$ nm[40]: $\Delta\alpha=20.4$ Å^3. We will suppose in the following that the dispersion of $\Delta\alpha$ between 541.6 and 632.8 nm may be neglected, and use the approximate expression

$$(\overline{n^2}+2)/(n_e+n_0)\simeq(\bar{n}^2+2)/2\bar{n}$$

since it introduces an error smaller than 4%.

The resulting value of a is $a=0.4\times10^6\ \mathrm{erg\ cm}^{-3}$; b and c are related to a by the following equations:

$$b=3a(T_K-T^*)/S_K\,,\quad c=\tfrac{2}{3}a(T_K-T^*)/S_K^2\,.$$

We can give a rough estimate of b and c if we use for S_K the value calculated by Maier and Saupe,[2] which proved not to be so far from those obtained from NMR.[41] Then $b\simeq5.6\times10^6\ \mathrm{erg\ cm}^{-3}$ and $c\simeq2.8\times10^6\ \mathrm{erg\ cm}^{-3}$. These numerical values will be of interest in Sec. V to validate some approximations made in Sec. II.

V. ANOMALY OF OPTICAL KERR CONSTANT: DISCUSSION

A. Adequacy of theoretical background

In Sec. IV, it was shown that the relaxation time of the optically induced birefringence varies with temperature in agreement with the mean-field law. This allowed us to fix the value of the second-order transition temperature T^*. On the contrary, the optical Kerr constant of MBPB seems to obey the $(T-T^*)^{-1}$-type law only when $T-T^*$ is less than a few degrees: about 4 °C for the first experiment ($\lambda_p=632.8$ nm) and 9 °C for the second ($\lambda_p=441.6$ nm). At higher temperatures, the decrease of B is slower than predicted by the mean-field law.[42] From Secs. III and IV, it seems that this discrepancy cannot be the consequence of experimental imperfections, but is probably due to the inadequacy of the theoretical background reviewed in Sec. II. First of all, we shall estimate the lower limit of the temperature from which the theory of Landau–de Gennes is self-consistent. Next, we shall criticize the simplification we made when applying the theory.

1. Critical behavior in vicinity of T_K

In the vicinity of T^*, both the correlation length and the relaxation time τ diverge. The fluctuations of the order parameter are large and their contribution to the free energy (1) are no longer negligible. Then, the mean-field approximation fails. A complete calculation of the fluctuations $\langle S^2(q)\rangle$ taking into account the third- and fourth-order terms of F is now necessary to estimate the range of temperature within which such effects must be expected. According to Stinson and Litster,[7] one finds

$$\langle S^2(q)\rangle\propto\frac{kT}{A}\left(1-\frac{3}{2}\frac{c}{V^*}\frac{kT}{A^2}+\frac{5}{6}\frac{b^2}{V^*}\frac{kT}{A^3}\right),$$

where $V^*=\tfrac{4}{3}\pi\xi^3$. Replacing a, b, and c by their numerical values, one obtains

$$\langle S^2(q)\rangle\propto(kT/A)(1+\Delta)\,,$$

with

$$\Delta\simeq-1.4\cdot10^{-2}(T-T^*)^{-1/2}+0.21(T-T^*)^{-3/2}\,.$$

For $T=T_K+1$ °C, $\Delta\simeq3\%$, which is comparable to the result of Stinson and Litster with respect to MBBA.[7] Δ decreases with increasing temperature and is always within the uncertainty of our measurements of the optical Kerr constant. Thus we may reliably expect no definite departure from mean-field behavior in the vicinity of the transition temperature.[43]

2. Influence of third- and fourth-order terms on induced birefringence

In order to calculate the expression of the Kerr constant B as a function of temperature, we have neglected the third- and fourth-order terms in the expansion (1). This simplification is valid if the induced order parameter is such that bS^3 and $cS^4\ll aS^2$.

From Sec. II, we know that

$$Q_{xx}=\tfrac{2}{9}[\Delta\chi/a(T-T^*)]E^2\,.$$

Then

$$Q_{xx}<10^{-3}(T-T^*)^{-1}\,.$$

One finds that the resulting error in S is less than 1% at $T=T_K$.

3. Influence of elastic terms

If the contribution to the free energy from gradients of the order parameter is taken into account $Q_{xx}(q,\omega)$ becomes

$$Q_{xx}(q,\omega)\propto\frac{1}{A}\,\frac{A/\nu}{i\omega+(A/\nu)(1+\xi^2q^2)}\,E^2(q,\omega)\,,$$

so the influence of the elastic terms becomes noticeable for the modes with a wavelength not too large compared to ξ.

Let us assume that the electric field is a Dirac pulse:

$$E^2(t, z) = \delta(t - z/c) .$$

Then

$$E^2(q, \omega) = \delta(q - \omega/c) .$$

The frequency associated with $q = 1/\xi$ is $\omega = c/\xi$. This frequency is about 10^{16} in the vicinity of T_K. Therefore the corresponding value of $Q_{xx}(q, \omega)$ is definitely negligible, and in conclusion the Kerr effect takes into account only the mode $q = 0$.

4. Other effects

Some other possible parasitic effects listed below have been pointed out and discussed by Prost[4]: (i) heating and electrostriction; (ii) hyperpolarizability: the calculations performed by Buckingham and Kielich[44] show that the contribution of the molecular hyperpolarizability is negligible. This was confirmed experimentally by Wong and Shen[10]; (iii) presence of free charges; (iv) coupling of the order parameter with polarization charges; (v) influence of the internal field: in fact, the order parameter induced in the optical Kerr effect is low enough for the anisotropy of the internal field to be completely negligible. The conclusions of Prost were that all these effects were probably too weak to explain the "anomalous behavior" of the optical Kerr constant of MBBA.

5. Conclusions

It appears that none of the approximations that we have made in the Landau–de Gennes theory is expected to fail at high temperatures. We must keep in mind that, up to now, the chosen theoretical background has been that of the isotropic-nematic phase transition. We have considered the fluctuations of the order parameter, characteristic of the phase transition, as the only relevant mechanism describing the response of the system to an intense electric field. Such a simplification is legitimate in the vicinity of the transition temperature, where these fluctuations are large enough to hide any noncritical mechanism coupled with the electric field.

When the temperature increases, the fluctuations of the macroscopic order parameter and, consequently, the nematogenic character of the liquid, decrease drastically. Then we may expect its behavior to approach that of ordinary liquids, that is, a supplementary noncritical contribution should appear at high temperatures.

B. Possible evidence of a supplementary contribution

1. Our results

a. Optical Kerr effect. In Figs. 3(a) and 3(b), B has been plotted vs $(T - T^*)^{-1}$, with the value of T^* taken from the relaxation studies. Both graphs obtained are very well fitted by the function

$$B = B_1 + B_2 , \quad B_1 = b/(T - T^*) , \quad B_2 = b'/T . \quad (14)$$

Since T varies only from 40 to 60 °C, B_2 may be considered as constant, within the experimental uncertainty in the measurement of B. Thus, we found $b' = 5634$ and $b = 392$ (a. u.) with $T^* = 40.5$ °C for the first experiment ($\lambda_p = 632.8$ nm), $b' = 1408$ and $b = 244$ a.u. with $T^* = 40.4$ °C for the second experiment ($\lambda_p = 441.6$ nm). Thus B_2 appears to be a constant or smoothly varying contribution to the Kerr constant, whereas $B_1 = b/(T - T^*)$ is the contribution related to de Gennes's theory, in the mean-field approximation. The numerical data mentioned above give two fairly different values of the ratio b'/b. We think this is a consequence of the repurification of the sample between the two experiments. This assertion will be discussed further at the end of Sec. V.

b. Depolarized Rayleigh scattering in the isotropic phase of MBPB. The experimental setup of this study has been described in an earlier publication.[40]

Let be R the whole scattered intensity. The results are shown in Fig. 3(c) under the form chosen by Stinson and Litster,[7,8] i. e., T/R as a function of temperature T. T/R appears to vary in a way quite similar to the one already observed by these authors: for temperatures exceeding T_K by at least 1 °C, the mean-field law seems to be obeyed, whereas close to T_K one observes some departure that could be related to the "pretransitional effects"[8] reviewed above. However, the value of T^* obtained from this curve, i. e., $T^* = 38.6$ °C is *definitely different* from the $T^* = 40.1$ °C that Lalanne[11,40] has obtained *on the same sample a very short time before* by studying the relaxation of the optical Kerr effect induced by picosecond waves. One must note that the difference between the two values (1.6 °C) is considerably larger than the experimental error (0.2 °C). Then, we try to fit the variations of R by a relation of the form

$$R = a + c(T/T - T^*) , \qquad (15)$$

where a, c, and T^* are adjustable parameters.

A least-squares calculation showed that Eq. (15) well describes the variations of R vs T [Fig. 3(d)]. We find that $a = 14$, $c = 1.80$ a.u., and $T^* = 39.95$ °C. One must note that the value of T^* determined in this way is now identical to that measured by

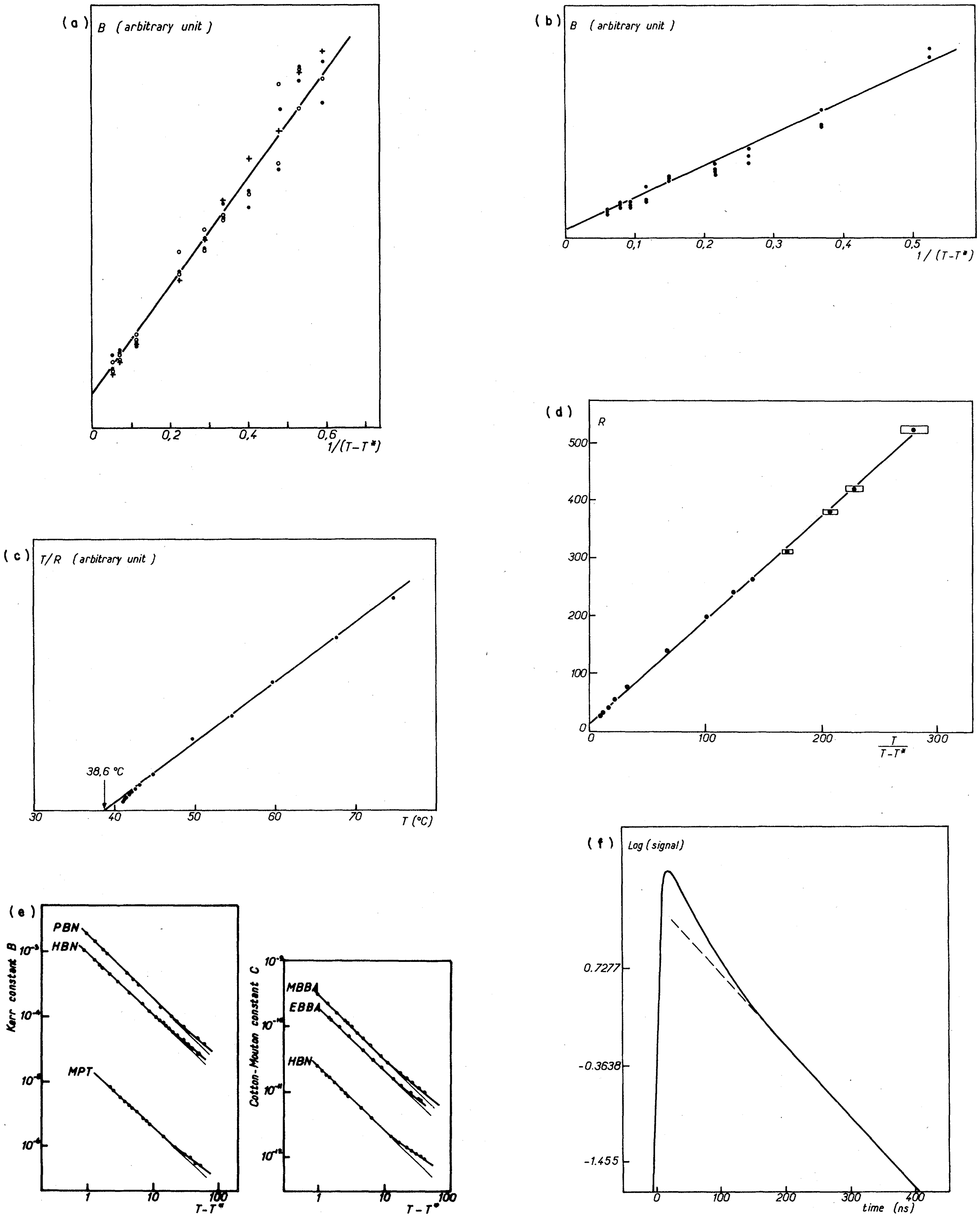

FIG. 3. (a) Optical Kerr constant vs $(T-T^*)^{-1}$, $\lambda_p = 632.8$ nm. $T^* = 40.5$ °C was yielded by the relaxation study. (b) Optical Kerr constant vs $(T-T^*)^{-1}$, $\lambda_p = 441.6$ nm. $T^* = 40.4$ °C was yielded by the relaxation study. (c) T/R as a function of temperature. (d) R vs $T/(T-T^*)$ with adjusted value of T^*. (e) Results reported by Filippini and Poggi. (f) Logarithm of the optical Kerr effect signal in the presence of two contributions of time constants τ_1 and τ_2; $\tau_1 = 250$ ns, $\tau_2 = 50$ ns.

the optical Kerr effect. The results obtained from depolarized Rayleigh scattering or from the optical Kerr effect in the isotropic phase of MBPB can be interpreted in the same way: both B and R behave as predicted by the Landau–de Gennes theory in the mean-field approximation, even close to T_K, on condition that one takes into account a supplementary contribution with no strong dependence on temperature.

2. *Other results*

a. Depolarized Rayleigh scattering. Recent depolarized Rayleigh scattering measurements in the isotropic phase of pentyl-cyano-biphenyl (5CB)[45] also show a departure from the Landau–de Gennes law at high temperatures.

b. Statical Kerr effect and magnetic birefringence experiments. J. C. Filippini and Y. Poggi[15] observe no departure from mean-field behavior in the vicinity of T_K but an "anomalous" increase of both the statical Kerr and Cotton-Mouton constants beyond the upper limit T_1 of the so-called "domain of pretransitional effects" [see Fig. 3(e)]. Their results clearly suppose the presence of an additive contribution with no critical thermal behavior to that of Landau and de Gennes.

C. Possible microscopic interpretation

The important values of the ratio b'/b, namely ~14 and ~6 in our two experiments, suppose that the supplementary contribution corresponds to a still very high anisotropy of the first-order molecular polarizability. Consequently it must result from a strong orientational coupling between molecules, roughly temperature independent, and quite different from that responsible for the long-range nematic order.

The experimental measurement of the ratio b'/b allows the evaluation of the squared value of the apparent optical anisotropy defined in Eq. (13). It can be shown that for top-symmetric molecules[9]

$$\gamma_I\gamma_p(1+J_A)=\gamma^2 Z\langle\tfrac{3}{2}\cos^2\theta_{ij}-\tfrac{1}{2}\rangle\,,$$

where Z is the "mean number of correlated molecules" and θ_{ij} the angle between the axes of symmetry of the molecules i and j. One finds, for MBPB and from depolarized Rayleigh scattering

$$Z\cdot\langle\tfrac{3}{2}\cos^2\theta_{ij}-\tfrac{1}{2}\rangle\simeq 5.$$

Let us now explain the variation of the measured values of the ratio B_2/B_1. The "supplementary contribution" to the Kerr effect or Rayleigh scattering is probably roughly constant from one sample to another of the same compound. On the other hand, the amplitude of the main contribution, arising from the fluctuations of the macroscopic order parameter, strongly depends on the chemical purity of the sample. This assertion is supported by the difference between the numerical values of the optical Kerr constant of MBBA found in our laboratory[4] ($b=0.33\times10^{-4}$ esu) and by Wong and Shen ($b=1.5\times10^{-4}$ esu). This difference suggests that the sample used by Wong and Shen was of much higher "quality" than that of Prost and Lalanne. In the same way, after our sample was repurified between the two experiments, the relative amplitude of the supplementary contribution was cut in half. Besides, note that the ratios c/a [Eq. (15)] and b'/b from the second experiment have similar values: $\frac{1}{8}$ and $\frac{1}{6}$, respectively. In both cases, the sample had been purified a short time before.

This orientational coupling is in this way found to be correlated over a distance much less than the correlation length ξ of the macroscopic order parameter-fluctuations; we now proceed to discuss the dynamics of reorientation of such correlated domains. Our assumption of a supplementary contribution must be coherent with the fact that the relaxation kinetics of the optically induced birefringence never showed any departure from the mean-field law. Let τ_1 and τ_2 be the characteristic time constants corresponding respectively to B_1 and B_2. The response of the system can be written

$$\frac{B}{\tau_1}y(t)e^{-t/\tau_1}=\frac{B_1}{\tau_1}y(t)e^{-t/\tau_1}+\frac{B_2}{\tau_2}y(t)e^{-t/\tau_2}\,. \tag{16}$$

The induced birefringence is proportional to the convolution product

$$(B/\tau_1)y(t)e^{-t/\tau_1}\times I_I(t)\,. \tag{17}$$

The "$\int S^{1/2}$" method gives directly

$$B=B_1+B_2\,. \tag{18}$$

Let us first assume $I_I(t)$ to be a Dirac pulse:

$$\tau_1\,,\,\tau_2\gg\delta \tag{19}$$

(where 2δ is the width at $1/e$ of the inducing pulse). Then, the method "of maxima" gives, from (16) and (17),

$$\frac{B}{\tau_1}=\frac{B_1}{\tau_1}+\frac{B_2}{\tau_2}\,. \tag{20}$$

Since both methods described above lead to the same results, Eqs. (18) and (20) imply $\tau_1=\tau_2$. Of course, this necessary condition is sufficient.

We must now discuss the case when inequality (19) is not fulfilled. The "anomalous" behavior of the optical Kerr constant taking place at temperatures where τ_1 is still much larger than the width of the inducing pulse, we may restrict ourselves to $\tau_2\ll\tau_1$, and $\tau_1\gg\delta$. Let $S_2(t)$ be the experimental signal corresponding to the supplementary contribution. The value of B_2 obtained by the "$\int S^{1/2}$" method is the surface $\int_{-\infty}^{+\infty} S_2^{1/2}(t)dt$. Besides, for temperatures not close to T_K, B_1 and B_2 are of comparable magnitudes. Therefore

$$\max S_2^{1/2}(t)\tau_2 \sim B_1 ,$$

and for $\tau_2 \ll \tau_1$

$$\max S_2^{1/2}(t) > B_1/\tau_1$$

We then see that, if $\tau_2 \ll \tau_1$, the supplementary contribution should appear as a sharp peak above the slow relaxation of time constant τ_1. This conclusion is illustrated in a more quantitative manner by the computed curve of Fig. 3(f). It is clear that such an effect does not appear anywhere on the recorded signal [see for instance Fig. 2(c)].

Thus, we think that the coupling related to B_2 is not definitely affected through the nematic-isotropic phase transition, and that it is correlated over a distance much less than the correlation length ξ of the macroscopic order-parameter fluctuations. Such a behavior suggests that the coherence time of the local order orientational fluctuations is *much larger* than the Landau–de Gennes time τ.

The existence of a coupling with the aforestated characteristics was reported by Leadbetter *et al.*[46] from x-ray observations. Their study was devoted to the nematic and isotropic phases of nonsmectogen compounds (MBBA, EBBA, 5CB, and 7CB). The microscopic behavior of such compounds is then probably similar to that of MBPB. In the nematic phase one observes a strongly anisotropic local order that can be characterized by means of two correlation lengths: L_z along the texture axis and L_r perpendicular to it. In the case of MBBA, L_z decreases down to about one molecular length with increasing temperature. L_r, on the other hand, is roughly temperature independent and equals about five molecular widths. It must be noted that the very same correlation length is found again in the isotropic phase: the local nematic structure remains unchanged through the nematic-isotropic phase transition.

The adjective "cybotactic" (χμβοσ: "cube," ταξισ: "ordering") was proposed in 1927 by Stewart and Morrow,[47] who had observed a similar local order in the case of fatty acids and aliphatic alcohols.

More recently, this term was used by De Vries[48] in the particular case of smecticlike microstructures inside the nematic phases of smectogen compounds. However, we think that the notion defined by Stewart and Morrow may be applied to the above-described local-order too. A cybotactic group must not be considered as a fixed crystalline microstructure, but rather as arising from some fluctuation of the distribution of molecular orientations. We think that the Kerr constant B_2 and the additive contribution a in depolarized Rayleigh scattering could be related to this kind of fluctuation.

VI. CONCLUSION

From optical Kerr effect measurements performed in the isotropic phase of MBPB, we have confirmed the adequacy of the de Gennes theory and of the mean-field approximation to describe the response of the isotropic phases of nematogens to an intense electric field. One must note that such a theory is also well adapted to the description of the optical Kerr effect of "pseudonematogens." Figure 4 reports the variation of $1/B$ vs temperature for the *p*-methyl benzoate *p*-*n* pentyl benzene (mBPB) in a narrow temperature range above the melting point and in the supercooled state. Such a critical behavior has been also recently evidenced by depolarized Rayleigh scattering in benzylidene compounds[49] and alkanes.[50]

But, from both optical Kerr effect and depolarized Rayleigh scattering it appears that *a contribution with no critical dependence on temperature must be taken into account*. As far as we know, this is the first time that such a contribution is accounted for. The magnitude of this supplementary contribution is likely to be roughly independent of the purity of the compound.

On the other hand, the magnitude of the main contribution to the optical Kerr constant, arising from the fluctuations of the macroscopic order parameter, seems to depend very much on the chemical purity of the sample. We think this could be the reason why departures from the $(T - T^*)^{-1}$-type law have been evidenced in static and optical Kerr effects,[18,15] in the Cotton-Mouton effect,[15] and in depolarized Rayleigh scattering.[40,45]

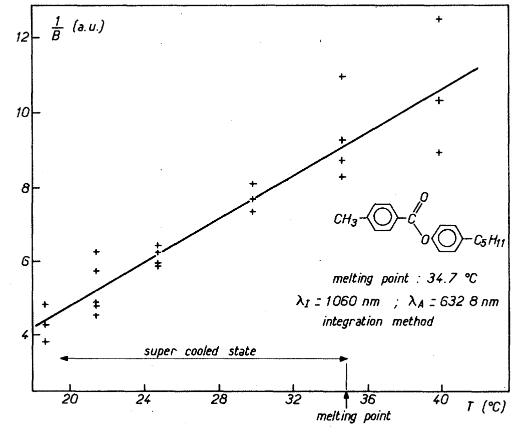

FIG. 4. Inverse of the optical Kerr constant of *p*-methyl benzoate *p*-*n* pentyl benzene vs temperature.

A microscopic interpretation involving the cybotactic local order in both nematic and isotropic phases of nematogens was suggested. This should stimulate further studies, especially with respect to the kinetics of local order fluctuations.

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APPENDIX A: FLUCTUATION-DISSIPATION THEOREM

We first briefly derive the fluctuation-dissipation theorem from quantum mechanics laws. We then give its classical formulation.

Suppose that a system is characterized by the average value of an observable A. We assume A to be time independent and of zero average value at thermal equilibrium:

$$\langle A\rangle_{\text{eq}}=0\,.$$

Let H_0 be the Hamiltonian of the system at equilibrium and $h(t)=-a(t)B$ a perturbation term, where $a(t)$ is a time-dependent scalar, and B a time-independent operator. To the first order in h, the average value of $\langle A\rangle$ under the influence of the perturbation is given by the convolution product

$$\langle A(t)\rangle=\int_{-\infty}^{+\infty}R_{AB}(t,t')a(t')dt'\,,$$

where $R_{AB}(t,t')$ is the impulse response of the system, equal to

$$R_{AB}(t,t')=(1/\hbar)\langle[A_I(t),B_I(t')]\rangle_{\text{eq}}y(t-t')\,.$$

where the index I refers to the interaction representation and $y(t)$ is the Heaviside function.

Let

$$S_{AB}(t,t')=\langle A_I(t)B_I(t')\rangle_{\text{eq}}\,.$$

It can be shown that $S_{AB}(t,t')$ depends only on $\tau=t-t'$, and that

$$S_{AB}(\tau)=S_{BA}(-\tau-i\beta\hbar)\,.$$

Moreover

$$\begin{aligned}R_{AB}(t,t')&=(i/\hbar)[S_{AB}(t,t')-S_{BA}(t',t)]y(t-t')\\&=R_{AB}(\tau)\,.\end{aligned}$$

Consequently

$$R_{AB}(\tau)=(i/\hbar)[S_{AB}(\tau)-S_{AB}(\tau-i\beta\hbar)]y(\tau)\,. \tag{A1}$$

This relation is the fundamental relation between the impulse response of the system and its fluctuations at equilibrium.

A. Classical limit: Nyquist's theorem

The classical limit of the above relation is obtained when $\hbar\to 0$, and is denoted by the superscript "cl" in what follows. One finds from (A1) that

$$\begin{aligned}R_{AB}^{\text{cl}}(\tau)&=\lim_{\hbar\to 0}R_{AB}(\tau)\\&=-\beta\frac{dS_{AB}^{\text{cl}}}{d\tau}\\&=-\beta\langle\dot{A}(t)B(t')\rangle y(t-t')\,.\end{aligned}$$

Let $R_{AB}^{\text{cl}}(\omega)$ the Fourier transform of $R_{AB}^{\text{cl}}(\tau)$:

$$R_{AB}^{\text{cl}}(\omega)=\int_{-\infty}^{+\infty}e^{i\omega\tau}R_{AB}^{\text{cl}}(\tau)d\tau\,.$$

Then

$$\begin{aligned}\text{Im}R_{AB}^{\text{cl}}(\omega)&=R_{AB}^{\text{cl}\,\prime\prime}\\&=\beta\omega\,\text{Re}\int_0^{+\infty}e^{i\omega\tau}S_{AB}^{\text{cl}}(\tau)d\tau\,.\end{aligned} \tag{A2}$$

If we further assume that $S_{AB}^{\text{cl}}(\tau)$ does not depend on the sign of τ, that is, $S_{AB}^{\text{cl}}(\tau)=S_{AB}^{\text{cl}}(-\tau)$, the spectrum of S_{AB}^{cl} is purely real,

$$R_{AB}^{\text{cl}}(\omega)=\tfrac{1}{2}\beta\omega S_{AB}^{\text{cl}}(\omega)\,.$$

This is the expression of the classical fluctuation-dissipation theorem. It relates, at thermal equilibrium, the dissipated energy at the ω frequency when A is excited by means of B, to the correlation function between A and B at the same frequency.

B. Generalization: spatial modes

More generally, the perturbation h is the energy transmitted to a volume Ω of the sample inside which A, B, and the conjugated field may vary. Then h is given by

$$h=-\int_\Omega a(r,t)B(r)d^3r\,.$$

If we assume that the problem does not depend on the origin of the space coordinates, the response $A(r,t)$ is found to be equal to the convolution product

$$A(r,t)=a(r,t)\times R_{AB}^{\text{cl}}(r,t)\,,$$

where

$$R_{AB}^{\text{cl}}(r,t)=-\beta\langle\dot{A}(r,t)B(0,0)\rangle_{\text{eq}}y(t)\,.$$

Let us now assume that the perturbation is a Dirac pulse and that the field E is parallel to $\hat{x}$. Then

$$a_{xx}(r,t)=\tfrac{1}{3}\Delta\chi(\omega_I)E^2\delta(r)\delta(t)$$

and

$$a_{\alpha\beta}(r,t)=0 \text{ if } \alpha \text{ or } \beta\neq x .$$

The induced birefringence at the probe circular frequency ω_p is then simply given by

$$\begin{aligned}\Delta n(\omega_p)&=[2\pi/n(\omega_p)]\Delta\chi(\omega_p)Q_{xx}\\&=-[2\pi/3n(\omega_p)]\Delta\chi(\omega_p)\Delta\chi(\omega_I)E^2R^{xxxx}(q,t),\end{aligned}\tag{A3}$$

or

$$\Delta n(\omega_p)=\frac{2\pi}{3n(\omega_p)}\Delta\chi(\omega_p)\Delta\chi(\omega_I)E^2\cdot\beta\left(\frac{d}{dt}\langle Q_{xx}(q,t)Q_{xx}(-q,0)\rangle_{\text{eq}}\right)y(t)\,.\tag{A4}$$

We see then that the induced birefringence, for $t>0$, is simply proportional to the derivative of the order-parameter fluctuations at equilibrium.

APPENDIX B

The Landau–de Gennes theory has allowed us to calculate $\Delta n(\omega_p)$ [Eqs. (6) and (8)]. From Eq. (A4) one can deduce the fluctuations of the system at equilibrium and the power spectrum of these fluctuations. According to Eq. (A2),

$$\operatorname{Im}R^{xxxx}(q,\omega)=\frac{\beta}{\Omega}\omega\operatorname{Re}\int_0^{+\infty}e^{i\omega t}\langle Q_{xx}(q,t)Q_{xx}(-q,0)\rangle_{\text{eq}}\,dt\,.$$

Let us now assume that the medium is illuminated by a monochromatic plane wave, linearly polarized along the direction $\hat{i}$, and propagating along the direction defined by the wave vector $\vec{k}_i$. Let $I_{if}(q,\omega)$ be the scattered intensity of wave vector $\vec{k}_f=\vec{k}_i+\vec{q}$, and polarized along the direction $\hat{f}$. If the scattering volume Ω is small compared to the optical wavelengths, $I_{if}(q,\omega)$ is given by

$$I_{if}(q,\omega)=\frac{2}{\Omega}\operatorname{Re}\int_0^{+\infty}e^{i\omega t}\langle\delta\epsilon_{if}(q,t)\delta\epsilon_{if}(-q,0)\rangle_{\text{eq}}\,dt\,.$$

In the case of an isotropic phase of a liquid crystal, one chooses the orientational order parameter as the only relevant variable describing the fluctuations $\delta\epsilon$ of the dielectric permittivity[51]:

$$\delta\epsilon_{if}=\tfrac{2}{3}\Delta\epsilon Q_{if}\,.$$

Let $i=f=x$. Then

$$I_{xx}(q,\omega)=\tfrac{8}{9}(\Delta\epsilon)^2(1/\beta\omega)\operatorname{Im}R^{xxxx}(q,\omega)\,.$$

But, from Eqs. (6)–(8) and (A3),

$$\operatorname{Im}R^{xxxx}(q,\omega)=\tfrac{2}{3}(1/\nu)\omega[(A/\nu)^2+\omega^2]^{-1}\,.$$

Then

$$I_{xx}(q,\omega)=\tfrac{16}{27}kT(\Delta\epsilon)^2(1/A)(\Gamma/\Gamma^2+\omega^2)\,,$$

where $\Gamma=A/\nu$ is the half-width at half maximum, of the spectrum of the scattered light.

The above-written expression of $I_{xx}(q,\omega)$ shows no dependence on q. This is a natural consequence of neglecting both the elastic terms and the coupling of the order parameter with velocity gradients. These approximations are equivalent to the limit $q=0$, where the fluctuations of the order parameter preserve the symmetry of the system. We may then consider the fourth-rank tensor

$$\langle Q_{\alpha\beta}(t)Q_{\alpha'\beta'}(0)\rangle_{\text{eq}}=S^{\alpha\beta\alpha'\beta'}(t)$$

as defined in an isotropic space. It is well known that such a tensor has only 21 nonzero components, given by[52]

$$S_1=S^{\alpha\alpha\alpha\alpha}\,,\quad S_2=S^{\alpha\alpha\beta\beta}\,,\quad S_3=S^{\alpha\beta\alpha\beta}\,,\quad S_4=S^{\alpha\beta\beta\alpha}\,,$$

with the supplementary condition

$$S_1=S_2+S_3+S_4\,.$$

But $Q_{\alpha\beta}$ is symmetrical and of zero trace, so

$$S_3=S_4\,,\quad S_1=-2S_2\,.$$

In conclusion, the fluctuation tensor $S^{\alpha\beta\alpha'\beta'}(t)$ may be entirely defined from one of its components. For instance:

$$\langle Q_{xy}(t)Q_{xy}(0)\rangle=\tfrac{3}{4}\langle Q_{xx}(t)Q_{xx}(0)\rangle$$

and

$$I_{xy}(\omega)=\tfrac{4}{9}kT(\Delta\epsilon)^2(1/A)\Gamma/(\Gamma^2+\omega^2)\,.$$

This is the expression, in the limit $q=0$, of the spectrum measured in depolarized Rayleigh scattering.

APPENDIX C: INFLUENCE OF COUPLING BETWEEN ORDER PARAMETER AND VELOCITY GRADIENTS

In Sec. II we have ignored the coupling between the order parameter and the shear strains in the fluid. In Appendix C we show that the usual geometric conditions of an optical Kerr effect setup are such that the induced birefringence signal is independent of the existence of this coupling.

The phase difference $\Delta\psi$ induced along the Kerr cell of length l is proportional to

$$\int_{-\infty}^{+\infty}dx\int_{-\infty}^{+\infty}dy\int_0^{l}dz\,Q_{xx}(t,r)\,.$$

Let $Q_{xx}(t,q)$ be the spatial Fourier transform of $Q_{xx}(t,r)$. Integrating over the whole plane (x,y) is equivalent to taking into account only the $q_x = 0$ and $q_y = 0$ componants along x and y. Then

$$\Delta\psi \propto \int_0^l dz \int_{-\infty}^{+\infty} dq_z e^{iq_z z} Q_{xx}(t, q_z) .$$

In the presence of the electric field E, the system of Eqs. (3)–(5) becomes

$$\tfrac{1}{2}\sigma_{\alpha\beta} = \tfrac{1}{2}\eta(\partial_\alpha V_\beta + \partial_\beta V_\alpha) + \mu \frac{\partial Q_{\alpha\beta}}{\partial t}$$

$$-AQ_{\alpha\beta} - \tfrac{1}{3}\Delta\chi(E_\alpha E_\beta - \tfrac{1}{3}\delta_{\alpha\beta}E^2) = \mu(\partial_\alpha V_\beta + \partial_\beta V_\alpha) + \gamma \frac{\partial Q_{\alpha\beta}}{\partial t} ,$$

$$\rho \frac{\partial V_\alpha}{\partial t} = \partial_\beta \sigma_{\alpha\beta} - \partial_\alpha p$$

(the fluid is assumed to be incompressible: $\partial_\gamma V_\gamma = 0$). By means of a Fourier transform and for

$$q_x = q_y = 0 , \quad q_z \neq 0 , \quad E_y = E_z = 0 , \quad E_x \neq 0 ,$$

one gets

$$\tfrac{1}{2} i\omega\rho V_x = -\tfrac{1}{2}\eta q_z^2 V_x + \mu\omega q_z Q_{xy} ,$$

$$-AQ_{zz} + \tfrac{1}{9}\Delta\chi E^2 = -2\mu i q_z V_z + i\gamma\omega Q_{zz} ,$$

$$-AQ_{xz} = -\mu i q_z V_x + i\gamma\omega Q_{xz} .$$

Then $Q_{xz} = 0$ and $V_x = 0$. In the same way $V_y = 0$ and, since the fluid is assumed to be incompressible, $V_z = 0$. Consequently

$$-AQ_{xx} - \tfrac{2}{9}\Delta\chi E^2 = i\gamma\omega Q_{xx} .$$

This is the same equation as if there were no coupling between the order parameter and the flow velocity gradient.

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