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Nonlinear optics can sometimes be used as a probe to study phase transition in a material. For example, second-harmonic generation, which is very sensitive to symmetry change, has been used to monitor the phase transition in crystalline NH_4Cl [1] and quartz [2]. Here, we choose to discuss a case when the optical Kerr effect is used to probe the pretransitional behaviour of the isotropic → nematic transition in a liquid crystal [3]. The same method has been applied to the study of pretransitional behaviour in plastic crystals [4].

A nematic substance is composed of long molecules. They are randomly oriented in the isotropic phase, but become more or less aligned to a common axis in the nematic phase. We can consider the substance as an analog to a spin system with no spin polarity. Each molecule here plays the role of a spin. The liquid phase is then equivalent to the paramagnetic phase, and the nematic phase to the ferromagnetic phase. In a paramagnetic system, an applied magnetic field H can induce a spin alignment and hence a magnetization along the magnetic field. The induced magnetization M in the mean-field approximation obeys the well-known Curie's law

$$M = C_M H/(T - T_c) \qquad (1)$$

which exhibits a critically divergent behaviour as the temperature approaches a critical temperature T_c, where C_M is a constant. A close analogue exists in liquid crystalline materials. There, an applied optical field $E(\omega)$ can also induce a molecular alignment in the isotropic phase. However, since the field variation at optical frequencies is too fast for the molecules to respond, the induced molecular alignment is proportional to $|E(\omega)|^2$ rather than $E(\omega)$. We therefore have $|E|^2$ play the role of H, while the induced molecular alignment is manifested by the induced anisotropy δn in the optical refractive index. We then expect that δn should also obey the Curie's law

$$\delta n = C|E|^2/(T - T_c) \qquad (2)$$

where C is a constant and T_c is the critical temperature for a second-order isotropic → nematic transition in the mean-field approximation. (We should note that δn can also be induced by a dc electric field. However, the results are often more difficult to interpret because of the presence of ionic conduction in the medium which also affects the molecular alignment.)

Let us now give a more rigorous derivation of Eq. (2). We use Landau's theory of second-order phase transition to describe the pretransitional behaviour of the isotropic → nematic transition [3,5]. First, we define an order parameter Q by the relation

$$\delta\chi = \chi_{\perp} - \chi_{\perp} = Q\Delta\chi \qquad (3)$$

where $\chi_\perp$ and $\chi_\perp$ are the optical susceptibilities parellel and perpendicular to the applied linearly polarized field $\vec{E}$ (ω) respectively, and $\Delta\chi$ is the anisotropy in χ when all molecules are perfectly aligned in one direction. Since the average susceptibility is $\chi_o = (\chi_\perp + 2\chi_\perp)/3$, we have $\chi_\perp = \chi_o + 2Q\Delta\chi/3$ and $\chi_\perp = \chi_o - Q\Delta\chi/3$. Then, following Landau's theory, we can write the free energy per unit volume in the isotropic phase $(Q \ll 1)$ as

$$F = F_o + \frac{1}{2} AQ^2 + BQ^3 + DQ^4 - \frac{1}{4} \chi_\perp |E(\omega)|^2 \tag{4}$$

where $A = a\,(T - T_o)$ and a, B, and D are constant coefficients. At temperatures sufficiently far above the transition, we expect Q to be so small that the BQ^3 and DQ^4 terms in Eq. (4) become negligible. We can then readily obtain the Curie's law of Eq. (2) from minimization of F with respect to Q. We find

$$\delta n = \frac{2\pi}{n} \delta\chi = \frac{\pi(\Delta\chi)^2}{3\,a\,n} |E|^2/(T - T_c). \tag{5}$$

It turns out that in nematic substances, the BQ^3 and DQ^4 terms in F, which are responsible for the observed first-order isotropic → nematic transition in the medium, are negligibly small even when T is very close to the observed transition temperature T_k. In fact, in several substances, the observed T_k is only less than 1°C above the fictious critical temperature T_c.

We can also discuss the dynamics of the optical field-induced anisotropy. It is described by the simple equation 3-5

$$\nu \delta Q/\delta t = -\delta F/\delta Q \tag{6}$$

where ν is a viscosity coefficient. The solution of the equation is

$$Q(t) = \int_{-\infty}^{t} \left(\frac{\Delta \chi |E(\omega)|^2}{6\,\nu} \right) e^{-(t-t')/\tau}\, dt' \tag{7}$$

where

$$\tau = \nu/A = \nu/a(T - T_c) \tag{8}$$

is the relaxation time for the order parameter. Equation (7) shows that if $|E(\omega)|^2$ is a pulse shorter or comparable with τ, then at sufficiently large t, the order parameter Q, and hence the induced optical anisotropy $\delta n = 2\pi Q \Delta\chi/n$, will decrease exponentially with a time constant τ. From Eq. (8), we note that as T approaches T_c, the relaxation time increases rapidly as $(T - T_c)^{-1}$. This is again analogous to the well-known critical slowing-down behaviour of the induced magnetization in a paramagnetic crystal near the paramagnetic → ferromagnetic transition.

It is easy to see from Eq. (7) that by measuring the transient response of $\delta n(t)$ induced by $|E(\omega)|^2$ of a given pulse shape, we can find the constants $\chi_2^{(3)} \equiv (\Delta\chi)^2/6a(T - T_c)$ and τ from which we can deduce

$(\Delta\chi)^2/a, \nu/a$, and T_c. Note that $\chi_Q^{(3)}$ is a third-order nonlinear optical susceptibility which is connected to the optical Kerr constant K by $K = 2\omega\chi_Q^{(3)}/nc$ and to δn by $\delta n = 2\pi\chi_Q^{(3)}|E|^2/n$. Because of the critically divergent behaviour of $\chi_Q^{(3)}$ and τ, the field-induced δn and its relaxation time for an isotropic liquid crystalline material are much larger than those for an ordinary liquid, especially when the material approaches the isotropic → nematic transition.

The experimental arrangement for measuring δn (t) is quite simple . An intense laser pulse is used to induce the optical anisotropy or Q, while a weak CW laser beam is used to probe the induced optical anisotropy. Since τ for liquid crystalline materials is of the order of a few nsec or longer, the laser pulse needed for the experiment can be either a Q-switched or a weakly mode-locked one. Such experiments have been carried out for a number of nematic substances. Figure 1 shows, as an example, the experimental results and theoretical comparison of $\chi^{(3)}$ and τ as functions of temperature for a nematic substance MBBA (C_4H_9 - (C_6H_4) - CH:N- (C_6H_4) - CH_3). The curves clearly demonstrate the critically divergent behaviour of $\chi_Q^{(3)}$ ($\beta \equiv 2\chi_Q^{(3)}$ in Fig. 1) and τ as the temperature approaches the isotropic → nematic transition. We note that $\chi_Q^{(3)}$ and τ shown in Fig. are much larger than those of ordinary liquids. At $T - T_c = 5°C$, $\chi_Q^{(3)}$(MBBA) $= 2.7 \times 10^{-10}$ esu is almost 100 times larger than that of the well-known Kerr liquid CS_2 at room temperature and τ(MBBA) $\simeq$ 100 nsec is 5×10^4 times longer than that of CS_2. The large values of $\chi^{(3)}$ and τ seem to be the characteristic properties of liquid crystalline materials as shown in table I for a number of nematic substances[6]. For MBBA, τ varies from 40 to 800 nsec as $T - T_c$ changes from 14.3 to 0.9°C.

Isotropic liquid crystalline materials with their large optical Kerr constants and the temperature-dependent long relaxation time turn out to be ideal systems for investigation of self-focusing of light. Because of the large δn, a Q-switched laser pulse will self-focus readily in such a medium. By varying the temperature of an appropriate liquid crystalline material, it is now possible to change the relaxation time τ from a value much larger than the laser pulsewidth to a value shorter than the laser pulse width. This means that with the same Q-switched pulse, we can now study not only the quasi-steady-state self-focusing phenomenon ($\tau \ll$ pulsewidth) but also the transient self-focusing phenomenon ($\tau \gg$ pulsewidth) and the intermediate cases between the two. In fact, study of self-focusing in MBBA has so far yielded the only quantitative experimental results on transient self-focusing in a liquid[7]. In ordinary liquids, τ is in the picosecond range, and therefore, picosecond laser pulses must be used to observe transient self-focusing. However, the present picosecond technology is not yet advanced enough for us to study transient self-focusing quantitatively.

For a third-order nonlinear optical effect governed by a third-order nonlinear polarization $P^{(3)} = \chi^{(3)} |E(\omega)|^2 E(\omega')$, there is always a counterpart in light scattering. Thus, corresponding to the optical Kerr effect due to induced ordering, we have light scattering by order -

parameter fluctuation in an isotropic liquid crystalline material[3,8] Then, Eqs. (4) and (6) with $|E(\omega)|^2 = 0$ can again be used to describe the light scattering phenomenon. Since $|E(\omega)|^2 = 0$, there is no induced ordering. However, as a result of thermal fluctuations, the mean square value $\langle Q^2\rangle$ is not zero, but from the equipartition theorem applied to Eq. (4), is equal to KT/A. Consequently, the scattering light intensity is

$$I \propto \left(\frac{d\varepsilon}{dQ}\right)^2 \langle Q^2\rangle = \left(\frac{d\varepsilon}{dQ}\right)^2 \frac{kT}{a(T - T_c)} \qquad (9)$$

which shows the critically divergent behaviour as $T \to T_c$. The dynamic equation for Q governs the spectrum of the scattered radiation. Equation 6 with $|E(\omega)|^2 = 0$ is in the form of a relaxation equation, and therefore it leads to a Lorentzian spectral line centered at the incoming laser frequency. The half width of the Lorentzian line is given by

$$\Gamma = A/\nu' = a(T - T_c)/\nu. \qquad (10)$$

We have, as expected, $\Gamma = 1/\tau$ which shows a critical narrowing behaviour as $T \to T_c$. The results in Eqs. (9) and (10) have been experimentally verified by Stinson and Litster[7].

Light scattering by order-parameter fluctuation appears as an intense narrow spectral line (halfwidth $\lesssim$ 100 MHz) centered at the laser frequency. However, as one looks more carefully at the scattering spectrum, one would find another much broader and much weaker component also centered at the laser frequency but with its wings extended out to tens of a cm^{-1}.[9] Such a broad component actually exists in all liquids and is believed to be due to light scattering by fluctuations of individual molecular orientations. This is known as Rayleigh -wing scattering[10]. Now, for liquid crystals, there is apparently a dilemma, since the order parameter fluctuation is clearly also a fluctuation in the molecular orientation. How can the same fluctuation of molecular orientation give rise to both the narrow central component and the broad Rayleigh-wing component?

Qualitatively, the answer to the above question is simple. We remember that the Landau theory we have used is actually equivalent to the mean-field theory which takes into account only the average local-field correction. This can be seen as follows. Microscopically, the molecular orientation is induced by the local field

$$|E_{\ell oc}|^2 = |E(\omega)|^2 + V \qquad (11)$$

where V is due to molecular interaction. In the mean-field approximation, we have $V = \lambda Q$ with λ being a proportional constant. The average induced molecular orientation Q is proportional to $|E(\omega)|^2$, i.e., $Q = b(T)\,|E_{\ell oc}|^2$, For $|T - T_c| \ll T_c$, by defining $b(T_c) = 1/\lambda$ and expressing $b(T) = b(T_c) + (T - T_c)(db/dT)_{T_c}$ we can write

$$Q = \text{Constant}\ |E(\omega)|^2/(T - T_c) \qquad (12)$$

Equation (12) is of course the same as one would obtain from minimization of F in Eq. (4).

The above derivation essentially follows the derivation of the magnetic susceptibility for a paramagnetic crystal near phase transition taking into account the mean local-field correction. This shows that the results derived from the free energy F in Eq. (4) have not included the temporal and spatial dependence of the local field due to molecular interaction. Physically, the mean field approximation describes the molecular orientational fluctuations under the influence of an average local field and predicts only a single Lorentzian spectral line with critical behaviour for the scattered radiation. In a more rigorous treatment, we should take into account the local-field correction more rigorously. Then, the problem of N interacting molecules can be considered as a problem of N coupled oscillators (referring to the orientational motion) in the highly damped limit. It is well known that a system of N coupled harmonic oscillators has many resonant lines. In the highly damped limit, the resonant frequencies of these lines are negligible compared to the linewidths, but different lines have different linewidths. Consequently, we expect to find a series of Lorentzian lines with different linewidths centered at zero frequency. The narrowest line shows the critical behaviour arising from the average local-field correction, while the others are much broader and show no critical behaviour but more or less characteristics of orientational fluctuations of individual molecules. The more formal derivation of the above discussion is given in Ref. 11.

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Table I.

Compound	R	T_c(°C)	$\tau(T - T_c)$ (10^{-8} sec-°K)	$\chi_Q^{(3)}(T - T_c)$ (10^{-10} esu-°K)
$C_4H_9-(C_6H_4)-CH{:}N-(C_6H_4)-R$	CH_3	41.7	67	13.2
	C_2H_5	67.6	21	7.8
	CH_3	130.7	8.5	15
$RO-(C_6H_4)-N_2O-(C_6H_4)-OR$	C_2H_5	161.0	7.5	10.2
	C_5H_{11}	115.0	25	5.6
	C_6H_{13}	126.0	15	4.7
	C_7H_{15}	121.3	15	5.4

Table I. Critical transition temperatures T_c, orientational relaxation times τ and nonlinear susceptibilities $\chi_Q^{(3)}$ for various nematic liquid crystalline compounds.

REFERENCES.

1. I. Freund, Phys. Rev. Lett. 19, 1288 (1967).
2. J. P. Bachheimer and G. Dolino, Phys. Rev. B11, 3195 (1975).
3. G. K. L. Wong and Y. R. Shen, Phys. Rev. Lett. 30, 895 (1973); Phys. Rev. A10, 1277 (1974).
4. T. Bischfberger and E. Courtens 32, 163 (1974).
5. P. G. de Gennes, Phys. Lett. A30, 454 (1969); Mol. Cryst. Liq. Cryst. 12, 193 (1971).
6. E. G. Hanson (to be published).
7. T. W. Stinson and J. D. Litster, Phys. Rev. Lett. 25, 503 (1970).
8. G. K. L. Wong and Y. R. Shen, Phys. Rev. Lett. 32, 527 (1974).
9. N. M. Amer, Y. S. Lin and Y. R. Shen, Solid State Comm. (1975).
10. See, for example, I. L. Fabellinski, "Molecular Scattering of Light"(Plenum Press, New York, 1968)Chapters II and VIII.
11. C. Flytzanis and Y. R. Shen, Phys. Rev. Lett. 33, 14 (1974).

FIGURE CAPTION

Fig. 1 (a) Nonlinear refractive index ($\Delta n = \pi\beta|E|^2/n$) as a function of temperature for MBBA. Δ are experimental data from optical Kerr measurements and 0 are experimental data from ellipse-rotation measurements. The solid curve is given by $5.4 \times 10^{-9}/(T - T_c)$ with 314.7°K.(b) Relaxation time τ_L of the order parameter as a function of temperature for MBBA. The solid curve is the theoretical curve and the dots are the experimental data points (after G.K.L. Wong and Y.R. Shen, Phys. Rev. A10, 1277 (1974).

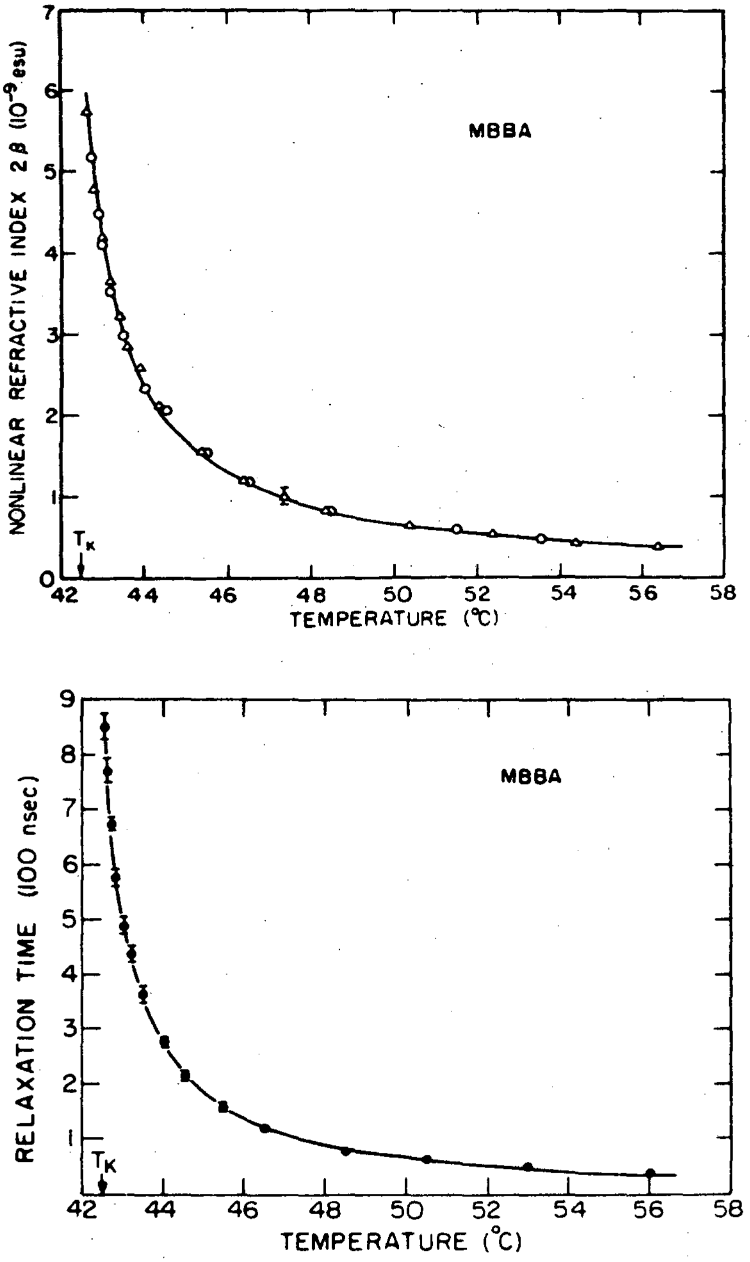

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Fig. 1

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