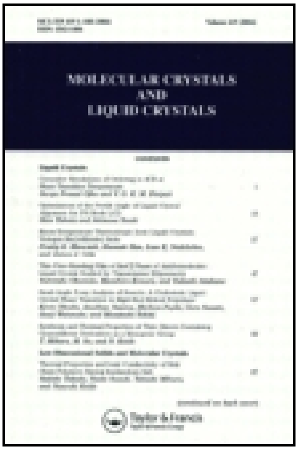

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Molecular Orientational Relaxation and the Thermal Nonlinear Refraction of Nematic Liquid Crystals

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Molecular Orientational Relaxation and the Thermal Nonlinear Refraction of Nematic Liquid Crystals

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Laser heating is known to make an important contribution to the nonlinear refraction of liquid crystals due to the large rate of change of the refractive index with temperature, *dn/dT*. There is a strong enhancement of *dn/dT* near the nematic-isotropic phase transition which is associated with the rapid variation of the nematic order parameter, S, with temperature. This has been seen to lead to a strong enhancement of the nonlinear refraction. However, if the nonlinear refraction is probed with laser pulses on the nanosecond time scale, incomplete relaxation of the order parameter during the pulse results in a reduction of the observed nonlinear refraction. The time scale for relaxation of the order parameter also shows a large peak near the phase transition temperature, so that for short laser pulses, the temperature dependence of the effective nonlinear refractive index, n_2, will be strongly influenced by the relaxation dynamics of the order parameter. This paper presents a simple model for the time evolution of the orientational order of a nematic liquid crystal subjected to heating by a gaussian laser pulse. By treating the orientational degrees of freedom with a phenomenological Landau-deGennes theory, and assuming that the other degrees of freedom equilibrate quickly compared to the pulse duration, it is possible to solve for the time dependence of the order parameter, and thus the indices of refraction. By defining an intensity weighted average of the change in index of refraction, an effective nonlinear refractive index can be extracted, such as would be measured in an experiment of the z-scan type. Using parameters which have been measured for the material 5CB, it is found that the slow relaxation completely cancels the enhancement of *dn/dT* near the phase transition, resulting in an effective n_2 which is nearly independent of temperature, for pulse durations less than a few tens of nanoseconds.

Keywords: nematic liquid crystal, non-linear refraction, liquid crystal

I. INTRODUCTION

The nonlinear optical response of liquid crystals has been the subject of much investigation recently.[1–8] In particular, the group of Palffy-Muhoray have undertaken to measure the nonlinear optical properties of various liquid crystalline materials, under a variety of temperatures, optical pulse durations, and optical field intensities.[3,4] These experiments made use of the z-scan technique[9,10] which relies on the self-refraction of a single pulse. The results of the measurements allow the samples to be characterized by a nonlinear refractive index, n_2, where the intensity dependent index of refraction is

$$n(E^2) = n + \frac{1}{2} n_2 E^2 \tag{1}$$

and a nonlinear absorption coefficient, β, where the intensity dependent absorption is given by

$$\alpha(I) = \alpha + \beta I \tag{2}$$

One of the simplest mechanisms which can contribute to the nonlinear refraction is a thermal mechanism, wherein linear absorption of energy from the optical field leads to heating of the sample, thereby changing its index of refraction. This mechanism is expected to lead to large effects in liquid crystals due to the rapid variation of the index of refraction with the temperature in these materials. This is especially true near the nematic-isotropic phase transition, where the variation of n with T is most rapid. This effect has been found to contribute significantly to a number of measurements; more detailed references and brief reviews can be found in References 1 and 2.

An estimate of the effective value of n_2 due to the thermal effect, as measured with a pulsed laser, can easily be obtained. For a sample with a linear absorption coefficient α, and heat capacity per unit volume C, in a laser pulse of peak intensity I_0 and duration τ, the change in temperature is $\Delta T \approx \alpha I_0 \tau / C$. The effective value of n_2 is approximately

$$\begin{aligned} n_2^{\text{eff}} &\approx \Delta n / E_0^2 \\ &\approx \frac{dn}{dT} \Delta T c n / I_0 \\ &= \frac{dn}{dT} \frac{\alpha \tau c n}{C} \end{aligned} \tag{3}$$

where c is the speed of light and n is the linear index of refraction. All factors of order unity have been dropped for the purposes of this order of magnitude estimate. Equation (3) ignores the diffusion of heat. In the experiments under consideration, the laser pulse duration is much shorter than the time scale for diffusion of heat across the beam, so that diffusion of heat will be neglected in all the following. Note that the result, (3) depends explicitly on the pulse duration, τ, as well as on material properties. This is the reason for referring to the "effective" n_2.

It was concluded in References 1 and 3 that the observed nonlinear refraction for pulses of several millisecond duration was due to the thermal mechanism. This conclusion was based on comparison of the measurements with order of magnitude estimates from Equation (3) and, most important, the fact that the measured n_2

has a pronounced dependence on the temperature as the nematic-isotropic transition is approached from below. This strong temperature dependence is expected, since *dn/dT* is strongly temperature dependent for liquid crystals near the transition temperature. On the other hand, it was found[4] that for pulses of 7 ns duration, the observed n_2 was essentially independent of temperature, right up to the transition. This was taken as an indication that the dominant effect on that time scale did not have a thermal origin.

It should be pointed out, however, that Equation (3) is only appropriate if the heating is quasi-static, that is if the temperature changes slowly enough that the instantaneous change in index of refraction is related to the instantaneous change in temperature by the equilibrium coefficient, *dn/dT*. This will only be the case if the relaxation process which governs the change in index of refraction takes place on a time scale which is short compared to the pulse duration. If slow relaxation prevents the index of refraction from keeping pace with the instantaneous temperature during the optical pulse, then the observed n_2 will be reduced from the quasi-static prediction. For nematic liquid crystals, the variation of the index of refraction with temperature is primarily due to the change of the orientational order parameter, S, which is a measure of the degree of alignment of the long molecular axes, and is proportional to the dielectric anisotropy. It is the rapid variation of the order parameter with temperature near the transition which gives rise to the large value of *dn/dT*. In a sample subjected to rapid heating by a laser pulse, the order parameter may not maintain equilibrium with the instantaneous temperature as defined, for example, by the mean kinetic energy of the molecular centers of mass. In such a case, the observed nonlinear refraction will be reduced, to the extent that the order parameter, and thus the index of refraction, is unable to equilibrate during the pulse.

The free relaxation of the orientational order parameter has been observed directly[5,6,8] in the isotropic phase, and has been found to show a substantial pretransitional slowing down as the transition is approached from above. This is in accordance with a theory due to de Gennes.[11] The time scales involved are found to be on the order of hundreds of nanoseconds for temperatures close to the transition. On the basis of the theory of Reference 11, it is expected that a similar phenomenon will occur in the nematic phase, with a similar slowing down as the transition is approached from below. Thus, near the nematic-isotropic transition, the effective value of n_2 measured in the nanosecond regime will be determined by a competition between a large coefficient, *dn/dT*, and slow relaxation of the orientational order, leading to a long rise time for the thermal nonlinear refraction. In fact, this effect has already been seen experimentally by Armitage and Delwart,[7] who found that the rise time for a thermal diffraction grating showed a large increase as the nematic-isotropic transition was approached from below. They also attributed the effect to slow relaxation of S. Therefore, in order to predict the effective value of n_2 which will be observed with laser pulses in the nanosecond regime, and especially to account for the temperature dependence of n_2 near the phase transition, it will be necessary to include the appropriate relaxation dynamics in the description.

The purpose of this paper is to show how the relaxation dynamics of the orientational order can be accounted for in describing the thermal nonlinear refraction of a nematic liquid crystal. In particular, emphasis is placed on the role of slowing down of the orientational relaxation near the nematic-isotropic transition in determining the observed nonlinear response. In section II, some aspects of the theory of Reference 11 which underlie the subsequent treatment of both equilibrium and relaxation phenomena in nematic liquid crystals are reviewed. In section III, a simple model for the response of the orientation order of a liquid crystal subject to heating by an optical pulse with a Gaussian temporal profile is presented. This model is based on treating the non-orientational degrees of freedom as constituting a "bath" which is assumed to equilibrate quickly to a well-defined temperature. Energy taken up by the system from the optical pulse can exchange between the bath and the orientational degrees of freedom. The orientational order is taken to relax exponentially toward the equilibrium value associated with the instantaneous temperature of the bath. In this way, it is possible to obtain a closed system of equations for the time development of the order parameter and the bath temperature. By defining a suitable intensity weighted average of the change in index of refraction, one can obtain an effective n_2 which is appropriate for the types of measurements made in References 3 and 4. This is illustrated numerically using parameters for the material 5CB. It is found that the effective n_2 is strongly peaked just below the transition temperature for pulse durations greater than ~0.5 μs. However, for pulse durations in the nanosecond regime, slowing down of the orientational relaxation near the transition results in n_2 being nearly independent of temperature. Thus, the experimental observation[4] that the nonliner refraction of 5CB, as measured with 7 ns pulses is independent of temperature is not inconsistent with the nonlinearity being thermal in origin.

II. THERMAL PROPERTIES OF NEMATIC LIQUID CRYSTALS

According to the theory due to de Gennes,[11] the nematic phase is characterized by a symmetric, traceless tensor order parameter, Q_{ij} which is proportional to the anisotropic part of the dielectric tensor, ε_{ij}. In the cases of interest to us, the nematic order parameter tensor is found to be uniaxial in equilibrium, in which case, Q can be put in the form,

$$Q = \begin{pmatrix} -S/2 & 0 & 0 \\ 0 & -S/2 & 0 \\ 0 & 0 & S \end{pmatrix} \tag{4}$$

where S is the scalar order parameter. The temperature variation of S can be obtained from the free energy density,

$$\mathcal{F}(S, T) = \frac{1}{2} A(T) S^2 - \frac{1}{3} B S^3 + \frac{1}{4} C S^4 \tag{5}$$

by applying the condition

$$\frac{\partial \mathcal{F}}{\partial S} = 0. \tag{6}$$

where the temperature dependence of the coefficient, A, is given by

$$A(T) = a(T - T^*) \tag{7}$$

The free energy, $\mathcal{F}$, is that part of the total free energy which is singular at the nematic isotropic transition. $\mathcal{F}$ is associated with the orientational degrees of freedom of the long molecular axes, and in the subsequent development it is assumed that the other degrees of freedom can be treated as having a constant specific heat over the temperature range of interest. The truncation of Equation (5) at 4th order is somewhat arbitrary, but it has become conventional. This level of truncation provides a minimal description of the qualitative features of the nematic-isotropic transition. Applying the condition, (6) to (5) gives rise to two solution branches which satisfy the local stability condition,

$$\frac{\partial^2 \mathcal{F}}{\partial S^2} > 0. \tag{8}$$

For $T > T^*$, there is an isotropic branch with $S = 0$. A nematic branch exists for $T < T\dagger$, where

$$T\dagger = T^* + \frac{1}{4}\frac{B^2}{aC} \tag{9}$$

with an order parameter given by,

$$S(T) = S\dagger + \left(\frac{a}{C}(T\dagger - T)\right)^{1/2} \tag{10}$$

where

$$S\dagger = \frac{B}{2C}. \tag{11}$$

The actual nematic-isotropic phase transition occurs at a temperature, T_c between T^* and $T\dagger$ given by,

$$T_c = T^* + \frac{2}{9}\frac{B^2}{aC} \tag{12}$$

which is the temperature at which $\mathcal{F}$ goes to zero for the nematic branch.

In addition to the order parameter, another quantity which can be obtained from $\mathcal{F}$, which will be needed later, is the part of the specific heat associated with the orientational degrees of freedom,

$$
\begin{aligned}
C_0 &= -T\frac{d^2\mathcal{F}}{dT^2} \\
&= \frac{aTS}{2}\left[\frac{C}{a}(T\dagger - T)\right]^{-1/2} \qquad (13)
\end{aligned}
$$

where the total derivative notation has been used to indicate differentiation including the dependence of S on T.

The uniaxial order of the nematic phase gives rise to a uniaxial dielectric tensor with two eigenvalues, one for fields polarized parallel to the director and one for fields polarized perpendicular to the director, which can be written

$$
\begin{aligned}
\varepsilon_{\parallel} &= \varepsilon_1 + \varepsilon_2 S \\
\varepsilon_{\perp} &= \varepsilon_1 - \frac{1}{2}\varepsilon_2 S \qquad (14)
\end{aligned}
$$

These give rise to extraordinary and ordinary indices of refraction,

$$
\begin{aligned}
n_e &= \sqrt{\varepsilon_{\parallel}} \\
n_0 &= \sqrt{\varepsilon_{\perp}} \qquad (15)
\end{aligned}
$$

In all the numerical calculations that follow, the following set of parameters, which have been obtained for 5CB,[8] are used.

$$
\begin{aligned}
a &= 0.13 \times 10^6 \text{ J/Km}^3 \\
B &= 1.6 \times 10^6 \text{ J/m}^3 \\
C &= 3.9 \times 10^6 \text{ J/m}^3 \\
T^* &= 34^\circ\text{C} \qquad (16)
\end{aligned}
$$

Using this set of parameters in Equations (10) and (14), and by determining the values of ε_1 and ε_2 at the reference point,[12]

$$
\begin{aligned}
T &= 34.9^\circ\text{C} \\
n_e &= 1.632 \\
n_0 &= 1.532 \qquad (17)
\end{aligned}
$$

the temperature dependence of the indices of refraction shown in Figure 1 is obtained. In these plots, it has been assumed that the only temperature dependence of $\varepsilon_{\parallel}$ and $\varepsilon_{\parallel}$ comes through the dependence of S on T. Actually, ε_1 ε_2 will also depend on the temperature through their dependences on the molecular density. However, the most important part of the temperature dependence of the indices of refraction, particularly near the phase transition is due to changes of S with T. Since the focus of this work is mainly on the behavior near the phase transition, and on the dynamics of the orientational order, the density will be treated as being constant throughout.

Before proceeding, some comment regarding the accuracy of the numerical results is in order. It was remarked earlier that the truncation of the free energy expansion, Equation (5), at fourth order in S is somewhat arbitrary. This truncation has the result that the calculated behavior of S is not in very good agreement with direct observations[13] for temperatures more than a few degrees below the phase transition. The indices of refraction have a corresponding departure from measurements.[12] The value of S calculated from Equation (10) does not saturate properly in the nematic phase, and so the resulting indices of refraction are changing more rapidly at low temperatures than the experimentally measured ones. It should be possible to correct this by using a higher order expansion for Equation (5), but since there are not any widely agreed upon parameters for a higher order expansion, it seems preferable to live with the limitations of the fourth order expansion. The main focus here is on the behavior near the nematic-isotropic transition where Equation (5) should be adequate, but it should be borne in mind that the numerical results are not quantitatively accurate more than a few degrees into the nematic phase. It is expected that in general, the qualitative conclusions will be valid.

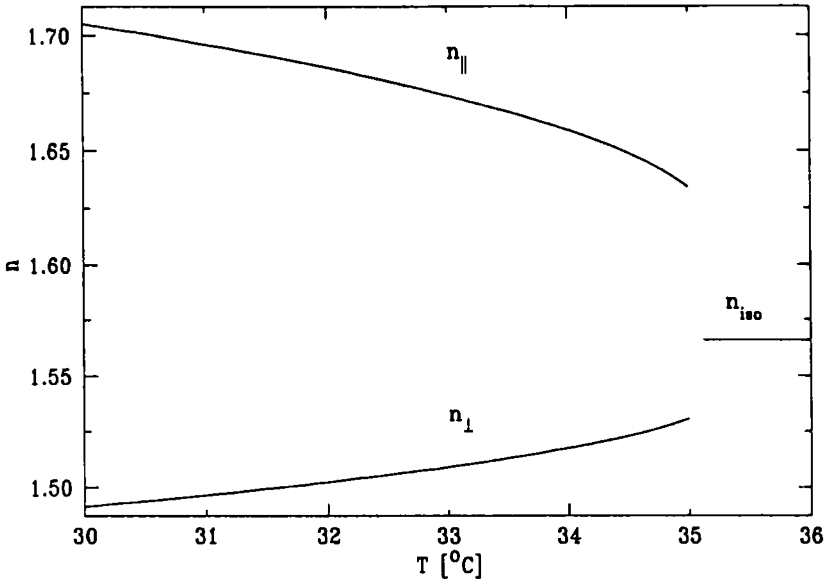

FIGURE 1 Temperature dependence of the indices of refraction, as obtained from Equations (10), (14) and (15).

Figure 1 shows that the indices of refraction have a strong temperature dependence close to the nematic-isotropic transition. According to Equation (3), this is expected to lead to a large effective n_2. It has been argued that this can be counteracted for short pulse durations, by slow relaxation of the orientational order close to the transition. Following Reference 11, the free relaxation of the order parameter is governed by

$$\nu \dot{S} = -\frac{\partial \mathcal{F}}{\partial S} \tag{18}$$

where ν is a viscosity coefficient, which can be related to the Leslie coefficient γ_1.[14] If Equation (18) is linearized about the equilibrium state, assuming a fixed temperature, one obtains

$$\nu \dot{S} = -\frac{\partial^2 \mathcal{F}}{\partial S^2}(S - S_0) \tag{19}$$

where S_0 is the equilibrium value of S at the given temperature. This leads to exponential relaxation of the order parameter to the equilibrium value, with a time constant

$$\tau_r = \nu \bigg/ \frac{\partial^2 \mathcal{F}}{\partial S^2} \tag{20}$$

which will be referred to as the isothermal relaxation time. This exponential relaxation behavior has been observed directly in the isotropic phase using the optical Kerr effect.[5,6,8] In the experiments, a strong optical pulse induces alignment of the molecules in an isotropic fluid. The subsequent decay of the orientational order is monitored by observing the induced birefringence with a weak probe beam. It is expected that the same description will hold in the nematic phase, although it will be more difficult to observe directly. Taking the value of ν from Reference 8, and using the free energy expansion given above, one obtains the behavior shown in Figure 2 for the temperature dependence of τ_r. In the isotropic phase, τ_r is simply $\nu/a(T - T^*)$, as has been observed in experiments. In the nematic phase, the temperature dependence of τ_r is more complicated, but τ_r tends to diverge as $(T\dagger - T)^{1/2}$ on approaching the transition from below. The large value of τ_r near the nematic-isotropic transition is associated with the fact that the transition temperature is very close to the critical temperatures, T^* and $T\dagger$. It has been assumed here that ν is independent of temperature. There is some evidence that ν has some temperature dependence,[5] however, this should be a weak correction to the rapid variation of τ_r near the phase transition.

III. ORIENTATIONAL RELAXATION

In treating the time dependence of the orientational order, and hence the refractive indices, of a liquid crystal sample subjected to heating by an optical pulse, the

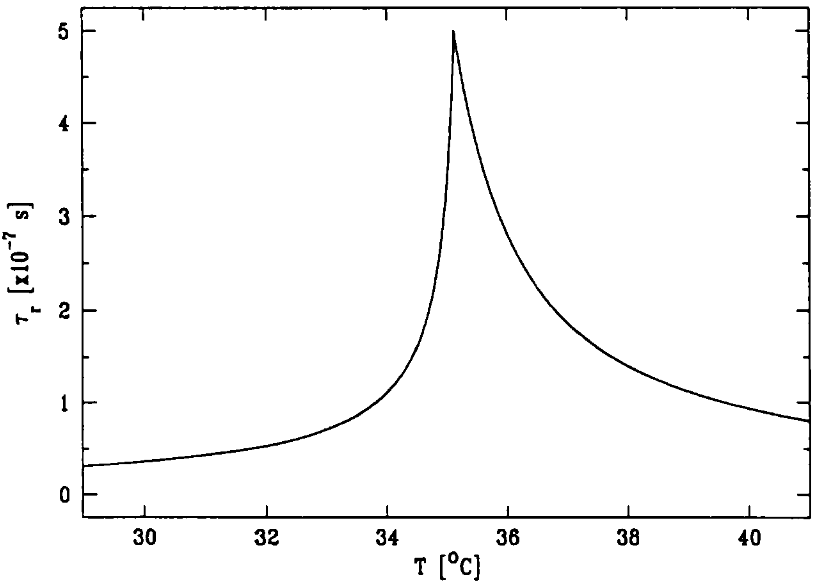

FIGURE 2 Temperature dependence of the isothermal relaxation time for fluctuations of the order parameter, S, as obtained from Equation (20).

simplification is adopted that all the non-orientational (vibrational, translational, etc.) degrees of freedom constitute a "bath" which equilibrates quickly to a well-defined temperature, T. This seems to be a reasonable assumption, since the time scales of interest here, tens to hundreds of nanoseconds, are long compared to the typical time scales for relaxation processes in liquids. This bath is assumed to be characterized by a specific heat, C_b, so that the balance of energy is given by,

$$\frac{du_0}{dS}\dot{S} + C_b\dot{T} = \alpha I \tag{21}$$

where α is the linear absorption coefficient and I is the intensity of the optical pulse. u_0 is the internal energy of the orientational degrees of freedom. In addition, the orientational order is assumed to relax toward the equilibrium value associated with the instantaneous temperature, according to Equation (18). It is assumed that the system is initially in an equilibrium state, characterized by $\partial\mathcal{F}/\partial S = 0$. By linearizing with respect to the quantities ΔT and ΔS, which are assumed to be small, then Equation (18) becomes,

$$\nu\dot{S} = -\frac{\partial^2\mathcal{F}}{\partial S^2}\left(\Delta S - \frac{dS}{dT}\Delta T\right) \tag{22}$$

where all coefficients, such as $\partial^2\mathcal{F}/\partial S^2$ should be understood as being evaluated at the initial state.

The first order system, Equations (21) and (22), can be solved straightforwardly, giving

$$\Delta S(t) = \frac{dS}{dT}\frac{\alpha}{C_b}\frac{1}{\tau_r}\int_{-\infty}^{t} dt'\, e^{-(t-t')/\tau'}F(t') \tag{23}$$

where F is the fluence, the time integral of the intensity,

$$F(t') = \int_{-\infty}^{t'} dt''\, I(t'') \tag{24}$$

and the time constant, τ' is related to the isothermal relaxation time, τ_r, by

$$\tau' = \tau_r \frac{C_b}{C_b + C_0} = \tau_r \frac{C_b}{C_t}\,. \tag{25}$$

Here C_t is the total specific heat, which is the sum of the part associated with the orientational degrees of freedom, which is calculated according to Equation (13), and the part, C_b, associated with the other degrees of freedom, which is assumed to be temperature independent. The value used for C_b is 1.78×10^6 J/K m^3, which is extracted from the data of Reference 15 as the value of the specific heat a few degrees above the transition where it is nearly constant, and by assuming a density of 1.0 gm/cm^3.

In experiments with pulsed lasers, the optical intensity typically has a Gaussian temporal profile,

$$I(t) = I_0 e^{-(t/\tau)^2} \tag{26}$$

and this is assumed to be the case henceforth. With this assumption, the fluence is,

$$F(t) = \tau I_0 \frac{\sqrt{\pi}}{2}(1 + erf(t/\tau)). \tag{27}$$

If one defines

$$\Delta S_0 = \sqrt{\pi}\frac{dS}{dT}\frac{\alpha I_0 \tau}{C_t} \tag{28}$$

then the solution for ΔS can be written in the dimensionless form,

$$\Delta S(t) = \Delta S_0 g(t/\tau;\, \xi) \tag{29}$$

where $\xi = \tau'/\tau$ is the ratio of the time constant to the pulse duration, and the function g is defined to be

$$g(z;\, \xi) = \frac{1}{2\xi} \int_{-\infty}^{z} dz_1\, e^{-(z-z_1)/\xi}(1 + erf(z_1)). \tag{30}$$

It is straightforward to verify that as $z \rightarrow \infty$,

$$g(z,\, \xi) \rightarrow 1 \tag{31}$$

so that as $t \rightarrow \infty$, $\Delta S(t) \rightarrow \Delta S_0$, independent of the value of the time constant. It is also easy to show that for $\xi << 1$, that is for small values of the time constant,

$$g(z,\, \xi) \rightarrow \frac{1}{2}(1 + erf(z)) \tag{32}$$

so that in this case $\Delta S(t)$ is simply proportional to $F(t)$, reproducing the quasi-static limit. Using Equation (21) the time dependence of the temperature can also be expressed as

$$\frac{\Delta T(t)}{\Delta T_0} = \frac{1}{r}\left(\frac{F(t)}{F_0} - (1 - r)\frac{\Delta S(t)}{\Delta S_0}\right) \tag{33}$$

where $r = C_b/C_t$ and

$$F_0 = \sqrt{\pi}\alpha I_0 \tau$$

$$\Delta T_0 = \sqrt{\pi}\,\frac{\alpha I_0 \tau}{C_t}. \tag{34}$$

Equations (26), (27), (29) and (33) are illustrated numerically, for various values of ξ in Figure 3. The value of $r = C_b/C_t$ is needed to define the temperature. The value $r = 0.5$ is a typical value, and is used in all the plots of Figure 3 for illustrative purposes. In the plots, the fluence, temperature and order parameter are all normalized so that they approach 1 as $t \rightarrow \infty$. In Figure 3(a), the value of $\xi = \tau'/\tau$ is 0.1, so that the time constant is shorter than the pulse duration. In this case both the temperature and the order parameter follow the fluence very closely, and the system is nearly in equilibrium at all times. Figure 3(b) shows the case $\xi = 2.0$ so that the time constant is twice as long as the pulse duration. In this case there is a very noticeable departure from equilibrium. The order parameter is not able to keep pace with the fluence, and this means that the bath initially takes up more of the energy than would be the case in equilibrium, resulting in the bath overshooting its final temperature. The change in order parameter, and hence the refractive index, during the pulse is substantially reduced from the equilibrium response. The order parameter does not equilibrate until after the pulse has passed.

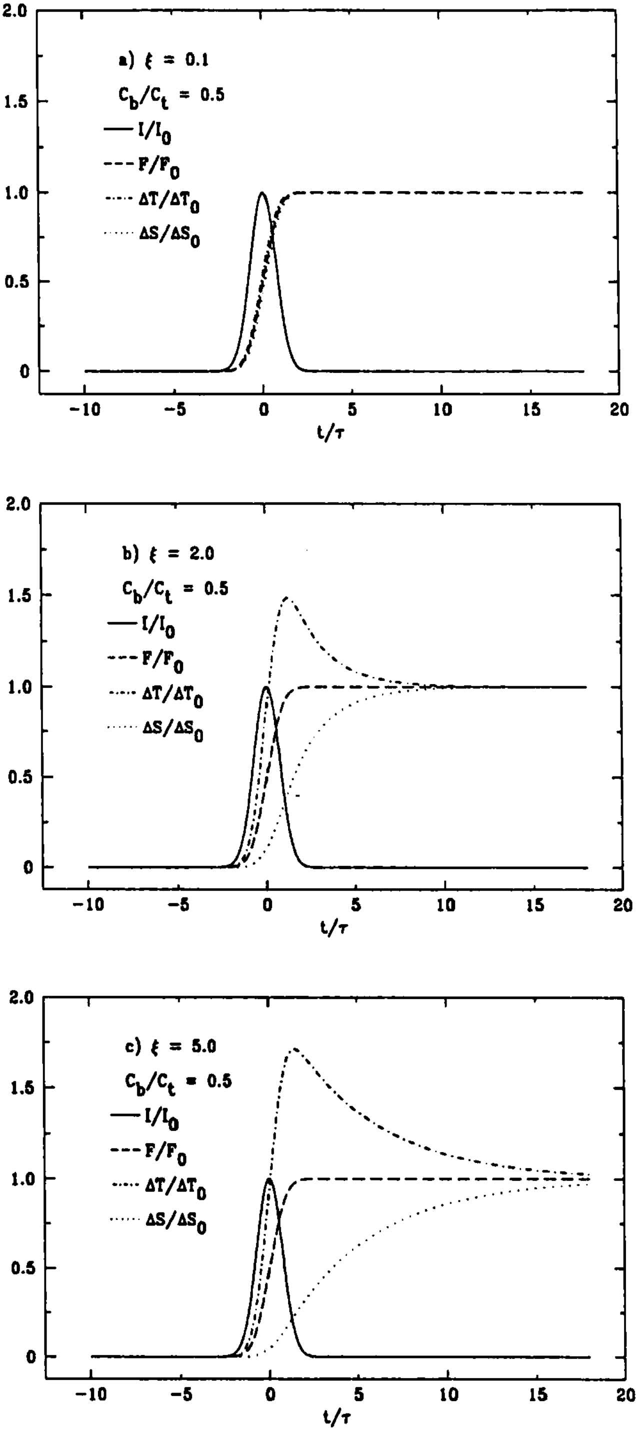

FIGURE 3 Time dependence of the order parameter and temperature, according to Equations (29) and (33). ξ is the ratio of the time constant, τ′, to the pulse duration, τ. Also shown are the pulse intensity and the fluence.

Figure 3(c) shows the case $\xi = 5.0$. This is qualitatively similar to Figure 3(b) but there is an even greater overshoot of the bath temperature and further suppression of the change in S during the pulse.

In an experiment, such as those of References 3 and 4, in which the self-refraction of a pulse is used to probe the nonlinear refraction, only the change of n which occurs during the pulse will effectively contribute to the measurement. Since in the z-scan measurements the signal is proportional to Δn, and the weight with which it is detected is proportional to I, it is reasonable to define the intensity averaged quantities

$$\overline{\Delta S} = \frac{\int dt\, I(t)\Delta S(t)}{\int dt\, I(t)} = \frac{1}{\sqrt{\pi}\tau} \int dt\, e^{-(t/\tau)^2} \Delta S(t) \tag{35}$$

and

$$\overline{\Delta n} = \frac{dn}{dS}\overline{\Delta S}. \tag{36}$$

Using Equation (29), $\overline{\Delta S}$ can be put in the form

$$\overline{\Delta S} = \Delta S_0 h(\xi) \tag{37}$$

where the function h is defined as

$$h(\xi) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dz\, g(z;\, \xi) e^{-z^2} \tag{38}$$

By comparing the intensity averaged change in index of refraction with that obtained from an instantaneous nonlinear refraction, it is possible to define an effective n_2. For an instantaneous nonlinearity, for which

$$\Delta n(t) = \frac{1}{2} n_2 E^2(t) \tag{39}$$

the intensity averaged change in index of refraction is

$$\overline{\Delta n} = \frac{2\pi I_0}{\sqrt{2}cn} n_2 \tag{40}$$

where c is the speed of light and n is the linear index of refraction. Using this relation, the effective nonlinear refractive index is defined in terms of the intensity averaged Δn as

$$n_2^{\mathrm{eff}} = \frac{\sqrt{2}cn}{2\pi I_0}\overline{\Delta n} \tag{41}$$

Together with Equations (37) and (36), this leads to

$$n_2^{\mathrm{eff}} = \frac{\sqrt{2}cn}{2\pi I_0}\frac{dn}{dS}\Delta S_0 h(\xi) \tag{42}$$

Using the definition (28) and the relation (15), one obtains

$$n_{2\parallel}^{\mathrm{eff}} = 2n_{2\parallel}^{0} h(\xi) \tag{43}$$

and

$$n_{2\perp}^{\mathrm{eff}} = -\frac{1}{2} n_{2\parallel}^{\mathrm{eff}} \tag{44}$$

where

$$n_{2\parallel}^{0} = \frac{c\epsilon_2}{4\sqrt{2\pi}}\frac{dS}{dT}\frac{\alpha\tau}{C_t} \tag{45}$$

which is just the value of $n_{2\parallel}$ in the quasi-static limit.

For convenience, the phenomenological parameters used in the calculations are summarized in Table I. Figure 4 shows the calculated results for n_2^{eff} along with n_2^0 for several values of the pulse duration. The value of the linear absorption

TABLE I

Summary of phenomenological parameters used in the calculations

a[a]	0.13×10^6 J/K m^3
B	1.6×10^6 J/m^3
C	3.9×10^6 J/m^3
T^*	34 °C
ν	7.3×10^{-2} kg/m s
n_e[b]	1.632
n_o	1.532
C_b[c]	1.78×10^6 J/K m^3

[a] Parameters for the deGennes free energy and viscosity are from Coles.[8]

[b] Indices of refraction at $T = 34.9$°C from Chu *et al.*[12]

[c] Non-orientational part of the specific heat obtained from the data of Iannacchione and Finotello[15] assuming a density of 1.0 gm/cm^3.

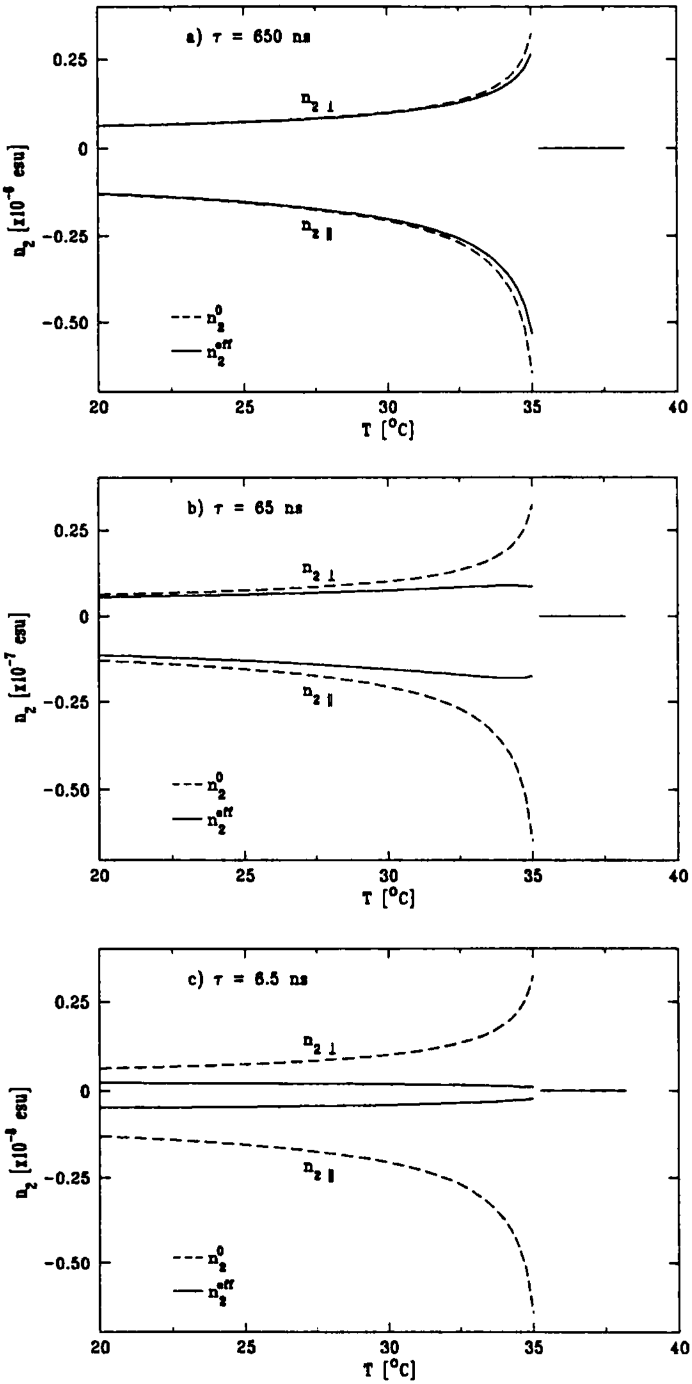

FIGURE 4 Temperature dependence of the effective nonlinear refractive index. Solid curves are n_2^{eff} calculated from Equation (43) which accounts for the effects of relaxation of the orientational order. Dashed curves are n_2^0, the quasistatic result. Laser pulse durations are a) 650 ns, b) 65 ns, and c) 6.5 ns.

coefficient, α, is taken to be 10 m^{-1}. The actual value of α for 5CB is not well known, so this value of α is chosen to agree in order to magnitude with measurements for related materials.[16] The value of α enters into the plots as an overall factor, through $n_{2\|}^{0}$ as given in Equation (45). Otherwise, the behavior shown in the plots is completely determined by independent measurements. Figure 4(a) shows the temperature dependence of n_2^{eff} and n_2^0 for polarization parallel to and perpendicular to the director for a pulse duration of 650 ns. At this time scale the behavior is practically quasi-static, and there is very little departure of n_2^{eff} from n_2^0. Figure 4(b) shows the same result for a pulse duration of 65 ns. In this case, the slow relaxation of the orientational order near the phase transition has mostly canceled the enhancement of n_2 due to the large value of dn/dT. Figure 4(c) shows the same thing again for $\tau = 6.5$ ns, which is the time scale probed in the experiments of Reference 4. In this case, there are significant effects of the finite relaxation time over the whole range of temperatures shown. The n_2^{eff} is nearly independent of temperature, and decreasing slightly, rather than increasing in magnitude on approaching the transition temperature. The order of magnitude of the calculated n_2 is consistent with the measurements of Reference 4, although, given the uncertainty of α, more detailed comparisons with the measured magnitude of n_2 are not meaningful.

IV. CONCLUSIONS

A simple formulation has been presented, which accounts for the relaxation dynamics of the orientational order of a nematic liquid crystal subjected to heating by linear absorption of energy from an optical pulse. This enables the calculation of the time dependence of the order parameter and thus the refractive indices. By defining a suitable intensity weighted average of the change in index of refraction, an effective nonlinear refractive index, n_2^{eff}, is extracted, which is comparable to what would be obtained from a measurement in a z-scan experiment of the type performed in References 3 and 4. The main result obtained here is that n_2^{eff} is essentially independent of temperature for pulses of several nanosecond duration. This is due to the fact that the relaxation time of the orientational order shows strong enhancement as the nematic-isotropic transition is approached from below, and for short pulses, this effect counteracts the strong increase of dn/dT near the transition.

With this result, it seems possible to explain many of the features of the observed nonlinear refraction in the nanosecond regime in terms of a thermal mechanism. For example, it was found[4] that for all the materials studied, $n_{2\|} < 0$ and $n_{2\perp} > 0$, as would be expected if the main effect were reduction of orientational order due to heating. In addition, experiments with two pulses separated by several nanoseconds showed a clear influence of the first pulse on the second, which is consistent with the accumulation of heat in the sample. The same type of temporal behavior was seen in a numerical simulation of pulse propagation in Reference 17 which assumed a thermal mechanism. The magnitude of the observed nonlinearity seems to be consistent with heating, up to the uncertainty in the linear absorption coefficient.

However, a complete description of the thermal nonlinear refraction requires some extensions of this work. The thermal variation of the density has been neglected, which has the effect that the calculated n_2 is zero in the isotropic phase. In the measurements, n_2 is found to be smaller, but still significant in the isotropic phase, indicated that the density variations make a non-negligible contribution. The present calculations satisfy

$$n_{2\perp}^{\mathrm{eff}} = -\frac{1}{2}\, n_{2\parallel}^{\mathrm{eff}} \tag{46}$$

strictly, whereas the experimental measurements satisfy this only approximately. This is partly due to the density variations, which will make a negative contribution to n_2 for both polarizations. It is also likely that anisotropy of the optical absorption coefficient α contributes to departures from Equation (46). Certain simplifications have been made here in order to focus attention on a specific point, and in order to avoid the introduction of a large number of adjustable parameters. The main result is expected to be independent of these simplifications.

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References

1. P. Palffy-Muhoray in *Liquid Crystals, Applications and Uses*, Vol. 1, ed. Birendra Bahadur (World Scientific, Singapore, 1990).
2. I. C. Koo, in *Progress in Optics* XXVI, ed. E. Wolf (North Holland, New York, 1988).
3. P. Palffy-Muhoray *et al.*, *Mol. Cryst. Liq. Cryst.*, **207**, 291 (1991).
4. L. Li, P. Palffy-Muhoray, M. A. Lee and H. J. Yuan in *Symposium on Optical Engineering and Photonics in Aerospace Sensing*, SPIE Proc., Orlando, FL, 1992; L. Li, H. J. Yuan, G. Hu, and P. Palffy-Muhoray, to appear in *Liq. Cryst.*
5. George K. L. Wong and Y. R. Shen, *Phys. Rev. Lett.*, **30**, 895 (1973).
6. J. Prost and J. R. Lalanne, *Phys. Rev. A*, **8**, 2090 (1973).
7. D. Armitage and S. M. Delwart, *Mol. Cryst. Liq. Cryst.*, **122**, 59 (1985).
8. H. J. Coles, *Mol. Cryst. Liq. Cryst.*, **49**, 67 (1978).
9. M. Sheik-bahae, A. A. Said and E. W. Van Stryland, *Optics Lett.*, **14**, 955 (1989).
10. Mansoor Sheik-bahae, Ali A. Said, Tai-Huei Wei, David J. Hagan and E. W. Van Stryland, *IEEE Journal of Quantum Electronics*, **26**, 760 (1990).
11. P. G. de Gennes, *Mol. Cryst. Liquid Cryst.*, **12**, 193 (1971).
12. K. C. Chu, C. K. Chen and Y. R. Shen, *Mol. Cryst. Liq. Cryst.*, **59**, 97 (1980).
13. J. W. Emsley, G. R. Lockhurst and C. P. Stockley, *Mol. Phys.*, **44**, 565 (1981).
14. P. G. de Gennes, *The Physics of Liquid Crystals*, Oxford University Press (Oxford 1974).
15. G. S. Iannacchione and D. Finotello, *Phys. Rev. Lett.*, **69**, 2094 (1992).
16. Shin-Tson Wu and Khoon-Cheng Lim, *Appl. Opt.*, **26**, 1722 (1987).
17. C. W. Greeff, J. Lu and Michael A. Lee, to appear in *Liq. Cryst.*