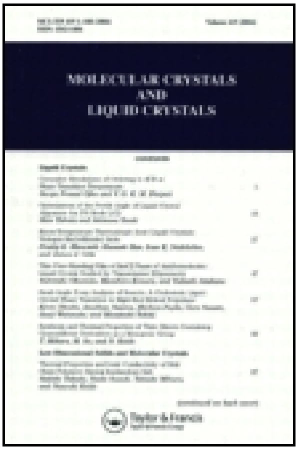

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Critical Behavior of the Thermal Diffusivity Near the NI Phase Transitions of n CB

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Critical Behavior of the Thermal Diffusivity Near the NI Phase Transitions of n CB

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Direct measurement of the thermal diffusivity of 8CB and 9CB is performed by Low angle forced Rayleigh scattering method.
Its critical behavior near the NI phase transition is compared to the well-known one of heat capacity at constant pressure.

Keywords: liquid crystals, forced Rayleigh scattering, thermal diffusivity

I. INTRODUCTION

Thermal flow techniques have long been used to measure transport coefficients.[1] However, near phase transitions, these techniques are time consuming and difficult to use. In the field of liquid crystal for instance, measurement of the thermal conductivity (Λ_{th})[2] were performed with temperature differences of approximately a few degrees, which made the procedure unapplicable close to transition temperature. On the other hand, photon-beating spectroscopy of Rayleigh scattered light can, in principle, lead to the determination of the thermal diffusivity $D_{th} = \Lambda_{th}/\rho\ C_p$, where ρ and C_p are the volumic mass and the heat capacity at constant pressure, but this method does not allow for a determination of each parameter separately.

A very simple and accurate optical method for obtaining both C_p and Λ_{th} has been proposed in the seventies. This method makes use of the well known Induced Thermal Lens (I.T.L.) effect. A pump wave is partially absorbed by the sample, causing local heating. This in turn produces a radial thermal gradient, resulting in a divergent thermal lens which blooms a non-absorbed probe wave (Figure 1b). This method has been successfully used to the measurement of small absorbances,[3] thermal conductivity near phase transitions in transparent liquids and solids,[4] thermal diffusivity[5] and thermal-diffusion

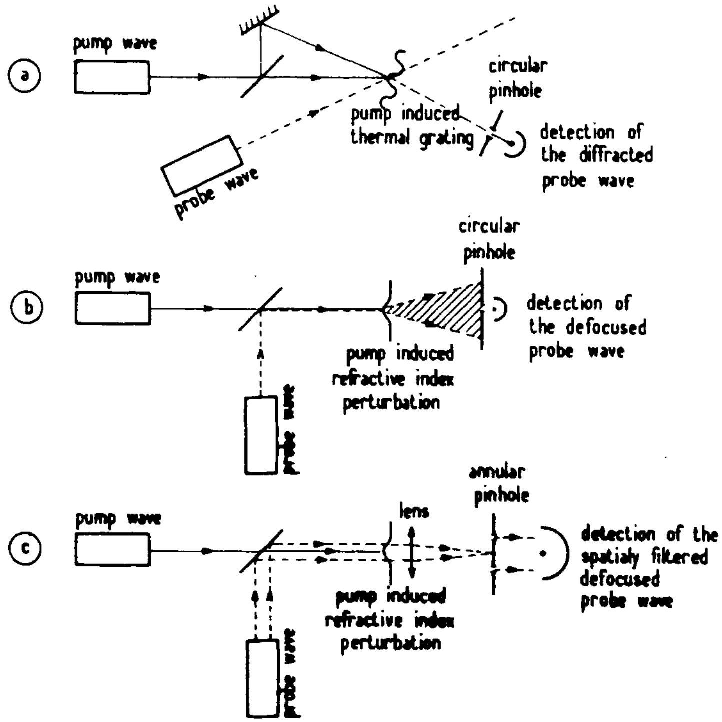

FIGURE 1 (a) Thermal dynamic grating (T.D.G) geometry
(b) Induced Thermal lens (I.T.L) geometry
(c) Low angle Forced Rayleigh Scattering geometry

ratio[6] in binary mixtures near the critical point. More recently, it has also been used for investigations in a microemulsion system.[7]

Thermal Dynamic Gratings (T.D.G.)[8] are a particular case of forced Rayleigh scattering, or laser induced gratings, and have also been used for the study of thermal conductivity and diffusivity in solids[9,10] in liquid crystals[11] and in micellar liquids.[12] In this method, a thermal grating is induced by the interference pattern of two coherent laser beams, and is read by a non-absorbed probe wave (Figure 1a).

As for the critical behavior near the NI transition of liquid crystals, definitely discrepant results have been reported. For instance, in the case of MBBA, T.D.G does not reveal any anomaly of Λ_{th}, even in the close vicinity of the NI transition temperature,[11] in agreement with classical thermal flow investigations,[2] while I.T.L measurements[13] show, in the isotropic phase, a critical increase of Λ_{th} of the form $(T-T_c)^{-0.65}$ (T_c is a critical temperature, slightly below T_{NI}).

The purposes of this paper are (i) to propose a new method for measuring D_{th} combining the advantages of I.T.L and T.D.G and avoiding their drawbacks, (ii) to report original experimental results concerning the variations of the thermal diffusivity with temperature of two n-alkylcyanobiphenyls, namely 8-CB and 9-CB, near their NI transition and (iii) to compare these results to recent measurements of the heat capacity at constant pressure performed on the same compounds,[14,15] and to already published results concerning other nematogens.[2,11]

II. EXPERIMENTAL

1. Optics

The basic advantages of the T.D.G method are:

—the capability to select one scattering wave vector $\vec{q}$, leading to a single exponential relaxation with a time constant τ given by:

$$\tau = 1/D_{th}\, q^2 \tag{1}$$

—the detection is performed on a dark background.

In the classical I.T.L arrangement, one measures the energy of the probe beam through a circular aperture beyond the sample. This amounts to monitoring the diameter of the Fresnel diffraction pattern of the transmitted probe beam. Clearly, the detection is performed upon a large background and moreover mixes wavevectors between zero and an upper limit corresponding to the aperture radius.

However, note that the I.T.L arrangement is simpler and involves wavevectors of values lower than in the T.D.G geometry. I.T.L relaxation signals are then slower than those of T.D.G and interaction lengths are usually larger in the I.T.L geometry than in the T.D.G one.

The principle of our method is shown in Figure 1c. A more detailed presentation is published elsewhere.[16] The left part of the Figure is the classical I.T.L geometry. A stabilized and modulated (rectangular pulses; 500 mW power; 50 ms duration; 1 Hz frequency) C.W. YAG laser is focused in the middle of the sample (2 mm depth). It plays the role of the heating pump wave, due to the weak absorbance of n CB at 1060 nm. The heating of the sample by this pump wave results in an axially symmetric modulation of the refractive index, which is felt by a C.W. He-Ne laser used as the probe beam (1 mW power at 632.8 nm). The detection is performed through an annular spatial filter of mean radius R, located in the image focal plane of a lens of focal length f. This amounts to selecting the modes of wave-vectors $\vec{q}$ such that:

$$|\vec{q}| = \frac{2\pi}{\lambda_{pr}} \frac{R}{f} \tag{2}$$

where λ_{pr} is the probe wavelength (632.8 nm). The probe beam intensity transmitted through the filter is measured by means of a photomultiplier tube. The transient signals are stored and digitalized for averaging. Experimental checks allow us to make the following assumptions:

— the observed I.T.L is entirely due to heat conduction
— the refractive index perturbation is proportional to the temperature jump ΔT
— the modification of the intensity distributions of the probe and pump waves is negligibly small compared to that of their phase distributions. With these assumptions, it can be easily shown[19] that, after the end of the heating pulse of duration τ_{pu}, the relaxation of the signal detected through the annular filter is given by:

$$\epsilon(R,t) = \epsilon^0(R)\,[1 - \exp(-D_{\text{th}}\,q^2 t)]^2 \tag{3}$$

where $\epsilon^0(R)$ is a time independent parameter given by:

$$\epsilon^0(R) = \frac{8f^2 P_{pr} a^2 b^2 P_{pu}^2 \left(\dfrac{\partial n}{\partial T}\right)^2 [1 - \exp(-ab)]^2 \exp - ({\omega_{pu}}^2 \pi^2 R^2/\lambda_{pu}^2 f^2)}{\pi^7 \rho^2 C_p^2 D_{\text{th}}^2 \omega_{pr}^2 R^4} \tag{4}$$

with:

P_{pr} and P_{pu}: powers of the probe and pump waves.
a: length of the sample.
b: absorbance of the sample.
ω_{pu} and ω_{pr}: beam-waists of the pump and probe waves in the sample.

Note that this method is just a time-resolved Spatial Fourier Spectrum of the I.T.L. This method is equivalent to T.D.G for small wavevectors ($q \lesssim 130\ cm^{-1}$), with the additional advantage that the wavevectors can be routinely changed in a range of several $10^2\ cm^{-1}$. Practically, it is a low-angle forced Rayleigh scattering method. The signal relaxes as a single exponential of time constant given by Eq. 1 over a very low background. By varying the mean diameter of the spatial filter, we have checked that τ is proportional to q^{-2} and obtained values of D_{th} with an uncertainty of a few 10^{-2}. Other checks and examples of agreement between experiments and predictions are published elsewhere.[17]

2. Sample

The sample is enclosed in a quartz cell (2 mm path length), located inside a temperature controlled aluminum block. Thermal contact is obtained by filling the space between the cell and the metal block with carbon tetrachloride, the absorbance of which is negligibly small at 1060 nm. Temperature fluctuations inside the sample are less than 0.01 K. The liquid crystal samples, 8 CB and 9 CB, have been purchased for British Drug House (ref. K24 and K27 respectively) and used without further purification. Orientation can be neglected in the samples.

III. RESULTS AND DISCUSSION

Figure 2 shows the thermal behavior of the relaxation time $\tau = (D_{th}\, q^2)^{-1}$ together with that of C_p for 8 CB.[14] The similarity of the two behaviors can be seen at first sight. One notes a drastic increase of τ on the isotropic side in the very close vicinity of the transition temperature (T_{NI}), however with no possibility for a quantitative analysis due to the lack of resolution. On the contrary, the variation of τ below T_{NI} is well resolved and can be analyzed in terms of a power law of the form:

$$\tau = \frac{A}{\alpha} t^{-\alpha} + \beta \qquad (5)$$

where t is the reduced temperature $T_c - T/T_c$.

In absence of an independent knowledge of T_c due to the first order character of the NI transition, no definite value of α can be found from the fitting of Eq. (5) to the experimental data. Acceptable values

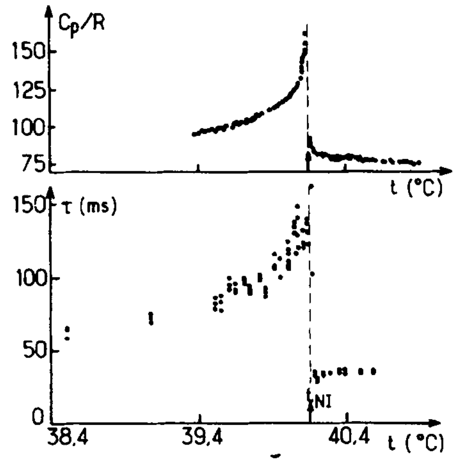

FIGURE 2 Variations of $\tau = 1/2\, D_{th}\, q^2$ with temperature near the NI transition of 8 CB. Comparison with the experimental results concerning C_p (Ref. 14). Length of the cell: 2 mm; power of the pump wave: 500 mW; $q = 153\ \text{cm}^{-1}$ duration of the heating pulse: 50 ms. $t_{NI} = (40.15 \pm 0.01)$°C.

of α fall in the range 0.1–0.5 (see an example on Figure 3). A similar conclusion has been drawn by THOEN[14] for the C_p data shown in Figure 2, in spite of the definitely lower experimental dispersion.

However, the shift between T_c and T_{NI} from the τ data is found in the range (0.05–0.35)K, while THOEN's one is in the range (0.02–0.06)K. In view of the fact that different experimental techniques about the pretransitional effects around the NI transition (heat capacity, thermal expansion, Rayleigh scattering, Kerr and Cotton-Mouton effects . . .) most often yield discrepant values for the reduced transition temperature, one may consider the above mentioned discrepancy as of minor significance and then that τ and C_p actually behave in the same way. Our observation that τ increases—in other words that D_{th} decreases—near T_{NI}, compares well with a similar behavior already pointed in T.D.G studies of BBOA and MBBA.[11]

Figure 4 shows the variation of τ in the isotropic phase of 9 CB in a range of 10K above T_{NI} (322.68 ± 0.01)K. The large increase of τ near T_{NI} is well resolved. The slow increase of τ at high temperatures can be accounted for by adding to the left side of (5) a regular contribution:

$$\tau = \frac{A}{\alpha} t^{-\alpha} + \beta + ct \tag{6}$$

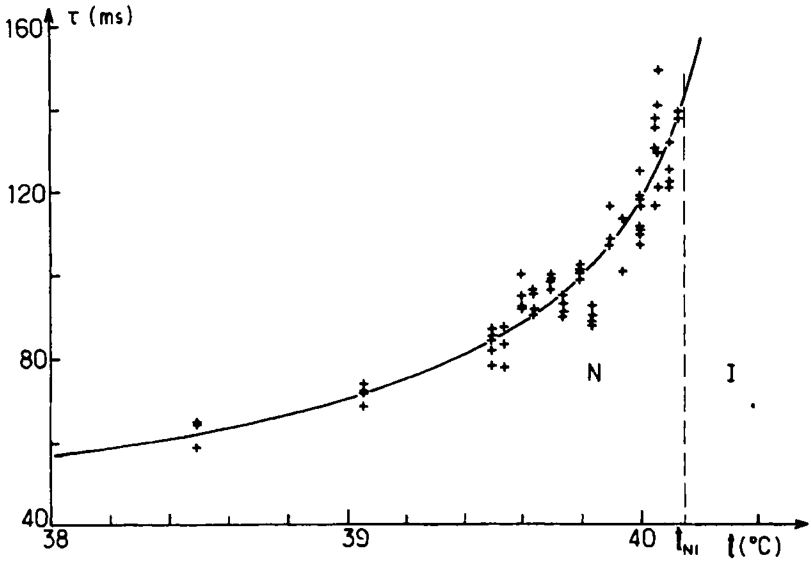

FIGURE 3 Example of fit of Eq. 5; sample: 2 mm of 8 CB in the nematic phase t_{NI} = (40.15 ± 0.01)°C. Results of the fit: T_c = 313.53K (40.38°C)

$$\tau_{ms} = 10.2 \left(\frac{T_c - T}{T_c}\right)^{-0.37} - 6.05$$

Of course, the difficulties for fitting Eq. 6 to the data are the same as for 8 CB. Again, we find an α exponent in the range 0.1–0.5, which is also in agreement with THOEN's values in the isotropic phases of 8 CB.[14]

The thermal conductivity is given by Λth = ρ C_p D_{th} by $\Lambda_{th} = \rho\, C_p\, D_{th}$. D_{th} is found from τ and C_p taken from Ref. (14). The specific mass ρ of 8 CB will be considered as a constant within the experimental temperature range of interest here. This simplification is based on the experimental observation[20] that the relative variation of ρ for 8 CB in a range of 2K below T_{NI} is only ~ 3.10^{-3}, e.g. well below our experimental uncertainty for *D*th. A similar observation has been made for 5 CB.[21] Figure 5 shows the variations of C_p,[14] *D*th (this work) and Γth (this work) for 8 CB on the nematic side of the transition. We have taken ρ = 0.9825 × 10^3 kg.m^{-3}, from reference 21.

Figure 5 seems to show that in spite of the relatively large experimental errors in τ and up to the nematic-isotropic, Λ_{th} does not

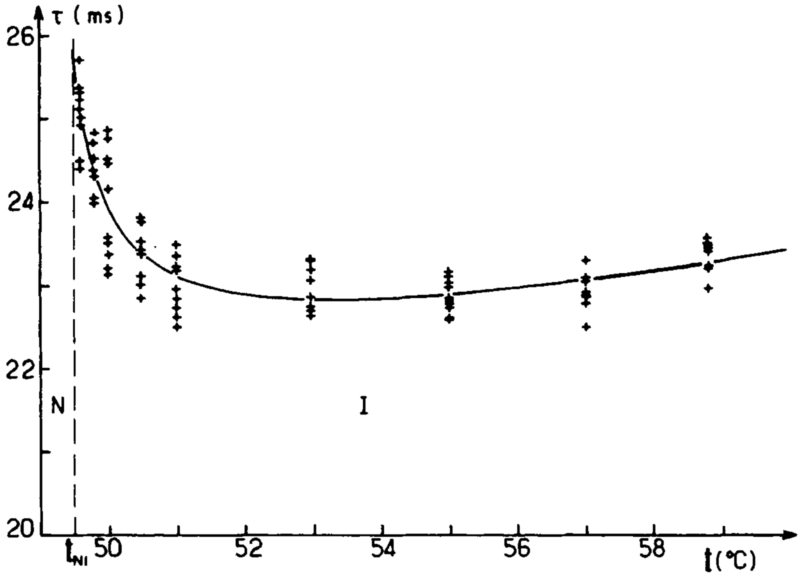

FIGURE 4 Example of fit of Eq. 6; sample: 2 mm of 9 CB in the isotropic phase t_{NI} = (49.53 ± 0.01)°C. Results of the fit: T_c = 322.45K (49.30°C)

$$\tau_{ms} = 0.486 \left(\frac{T-T_c}{T_c}\right)^{-0.33} + 20 + 57.7\,\frac{T-T_c}{T_c}$$

exhibit any critical increase, in agreement with results obtained either by thermal flow technique[2] or T.D.G.,[11] but in disagreement with I.T.L. investigations.[13]

IV. CONCLUSION

We have shown the capabilities of "Low Angle Forced Rayleigh Scattering" as an accurate and nonpolluting method for characterizing thermal transport properties in liquid crystals. We have found no critical increase of the thermal conductivity of 8 CB in the nematic phase close to the transition to the isotropic phase. This behavior seems to be due to the critical decrease of the thermal diffusivity near the transition which cancels out the critical increase of the heat capacity. But, of course, the best way to resolve the puzzle on Λ_{th} of the NI transition is performing a direct high-resolution measurement on Λ_{th} or a simultaneous measurement on heat capacity and thermal diffusivity as recently performed.[22,23]

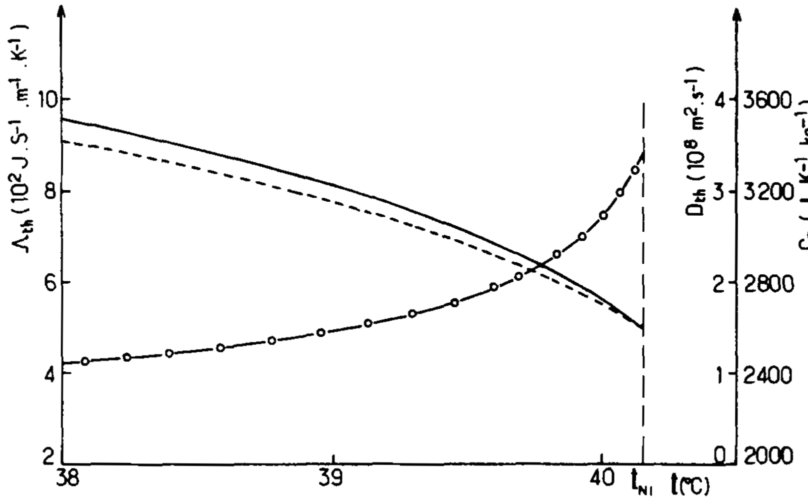

FIGURE 5 Sample: nematic phase of 8 CB [t_{NI} = (40.15 ± 0.01)°C]
length of the cell: 2 mm
ρ = 982.5 kg.m^{-3} (Ref. 14)
o C_p (Results Ref. 14)
— D_{th} values
— calculated values of Λ_{th}

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